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(12) **United States Patent**  
**Sampath et al.**

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(54) **METHOD OF MANUFACTURING AN ULTRAVIOLET LIGHT EMITTING ALGAN COMPOSITION AND ULTRAVIOLET LIGHT EMITTING DEVICE CONTAINING SAME**

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(73) Assignee: **The United States of America as represented by the Secretary of the Army**, Washington, DC (US)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 181 days.

(21) Appl. No.: **11/376,452**

(22) Filed: **Mar. 15, 2006**

**Related U.S. Application Data**

(60) Provisional application No. 60/663,144, filed on Mar. 18, 2005.

(51) **Int. Cl.**  
*H01L 21/00* (2006.01)  
*H01L 21/28* (2006.01)

(52) **U.S. Cl.** ..... **438/21; 438/29; 438/604**

(58) **Field of Classification Search** ..... **438/48, 438/54, 65, 69, 70, 29, 34, 35, 45, 46, 604; 427/569-579, 591, 598-599; 257/233, 292, 257/431-466; 428/641-642**

See application file for complete search history.

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*Primary Examiner*—Walter L Lindsay, Jr.

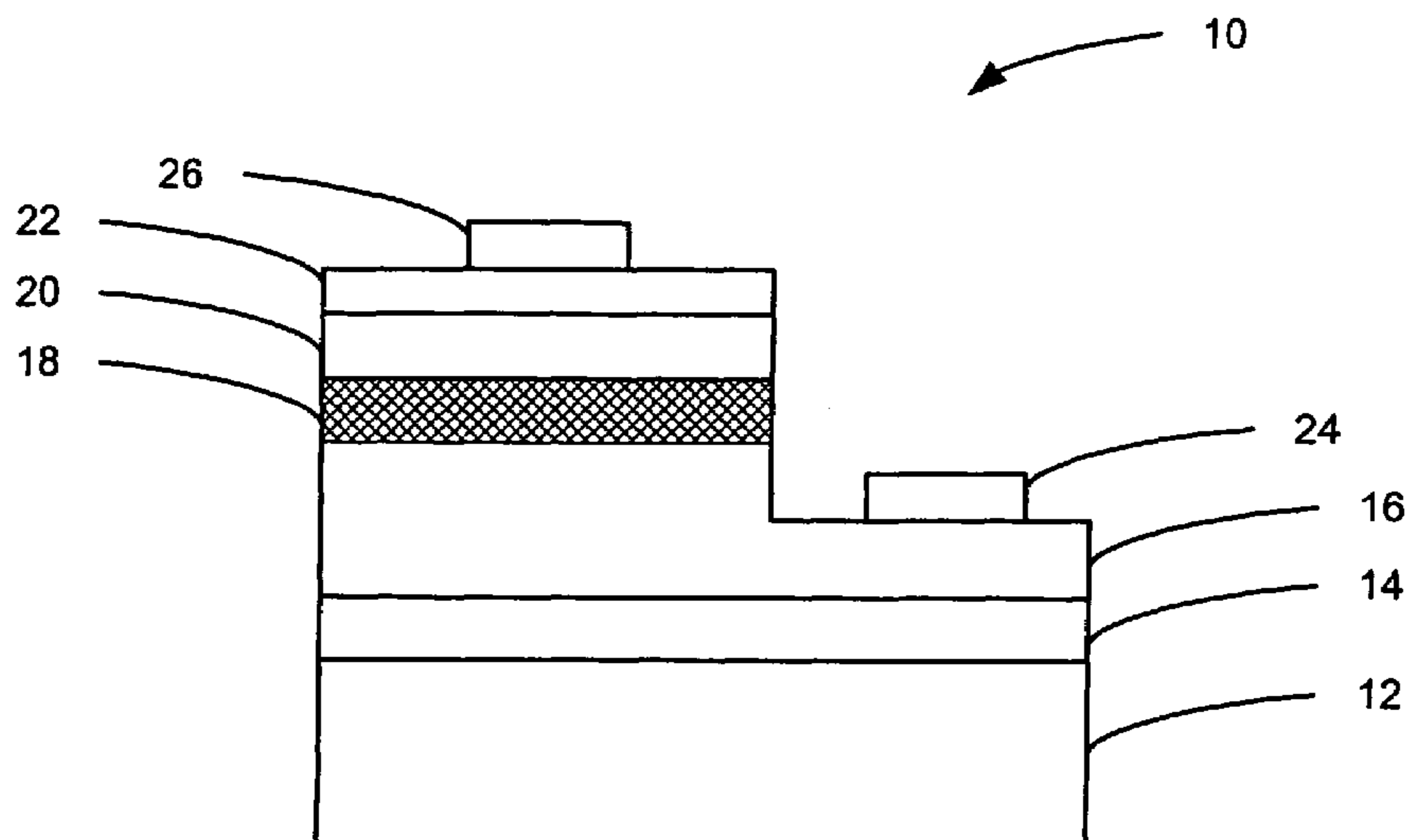
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(57) **ABSTRACT**

An AlGa<sub>N</sub> composition is provided comprising a group III-Nitride active region layer, for use in an active region of a UV light emitting device, wherein light-generation occurs through radiative recombination of carriers in nanometer scale size, compositionally inhomogeneous regions having band-gap energy less than the surrounding material. Further, a semiconductor UV light emitting device having an active region layer comprised of the AlGa<sub>N</sub> composition above is provided, as well as a method of producing the AlGa<sub>N</sub> composition and semiconductor UV light emitting device, involving molecular beam epitaxy.

**23 Claims, 27 Drawing Sheets**



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FIG. 1 (a)

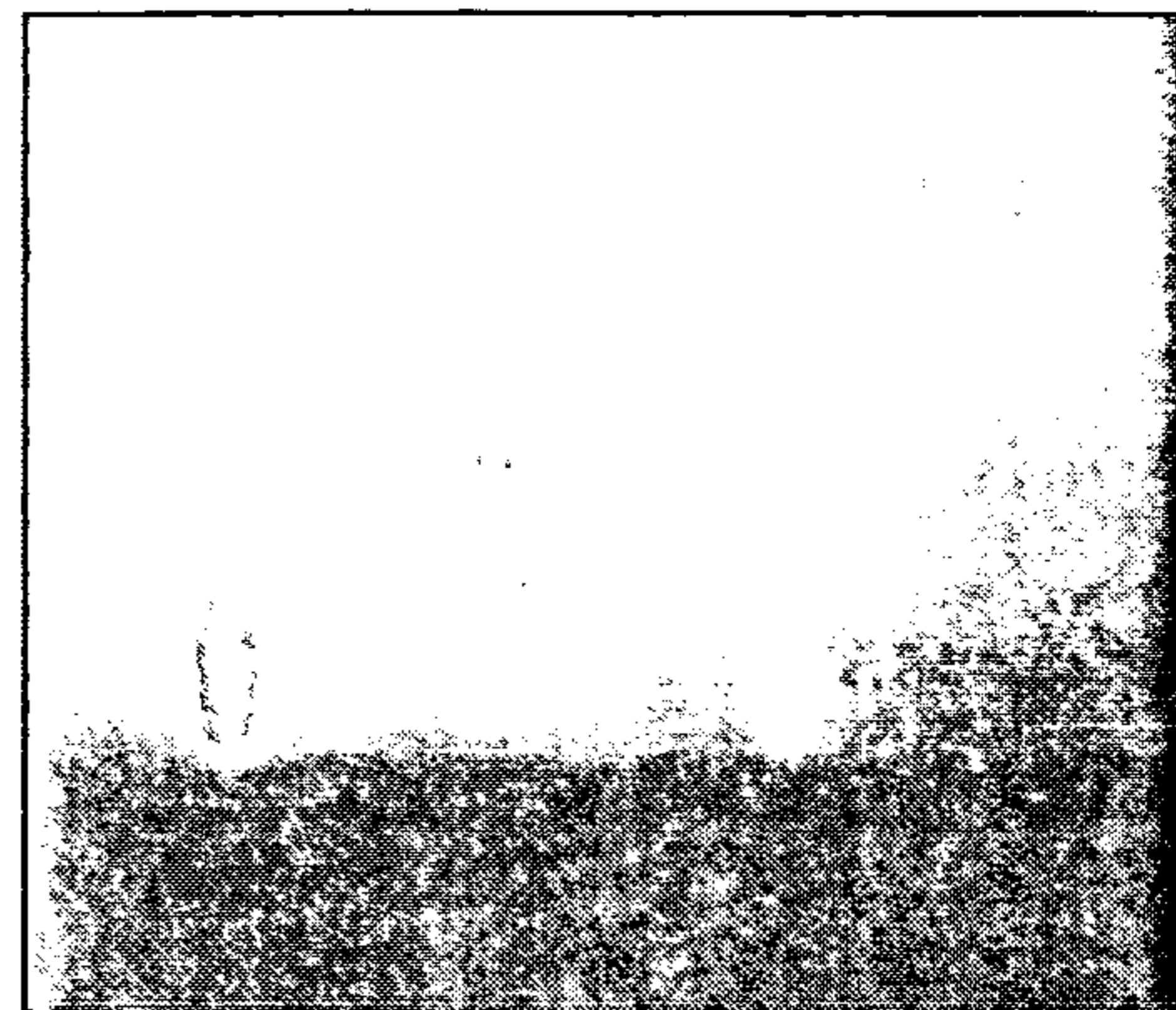


FIG. 1 (b)

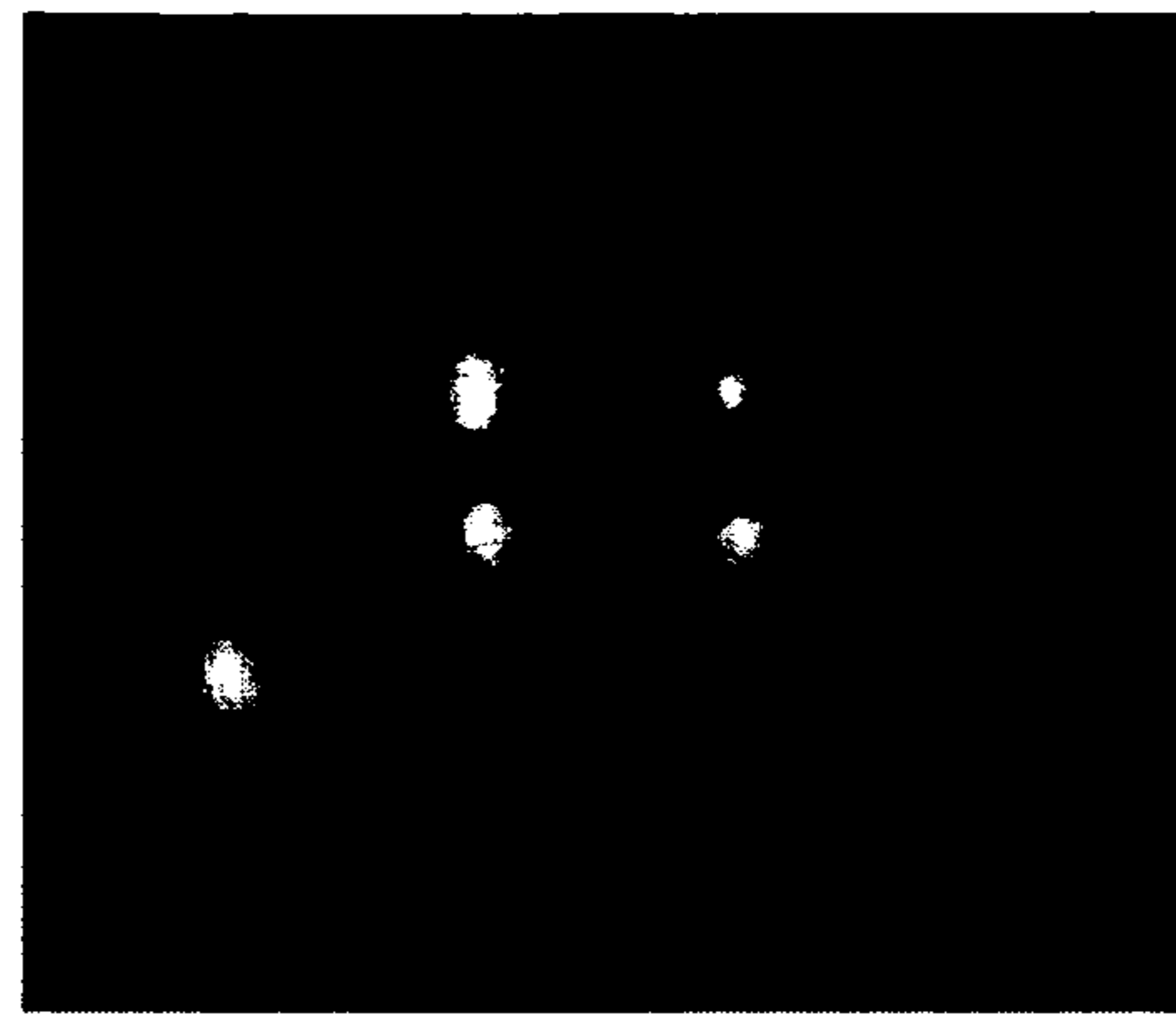
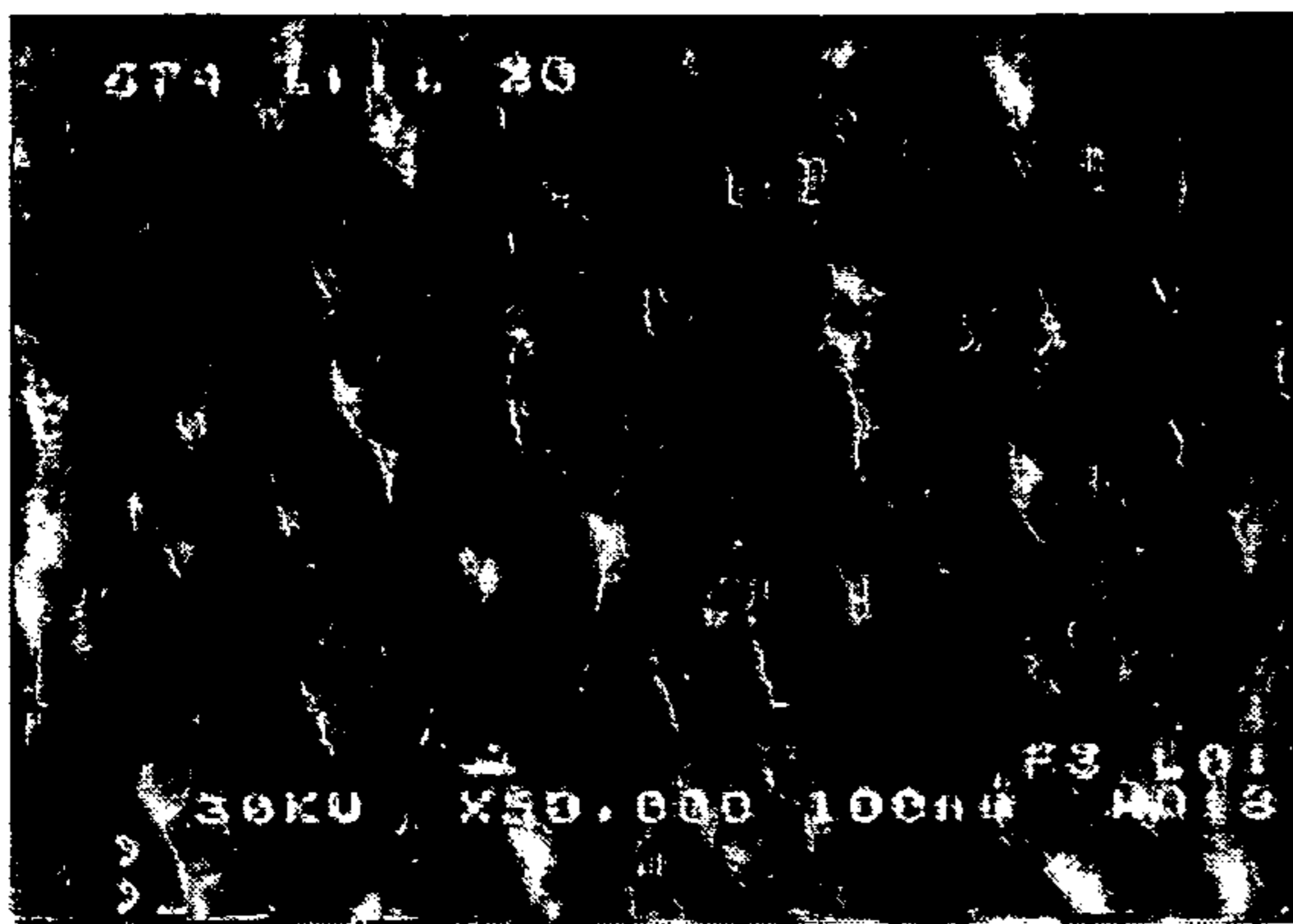


FIG. 2 (a)FIG. 2 (b)

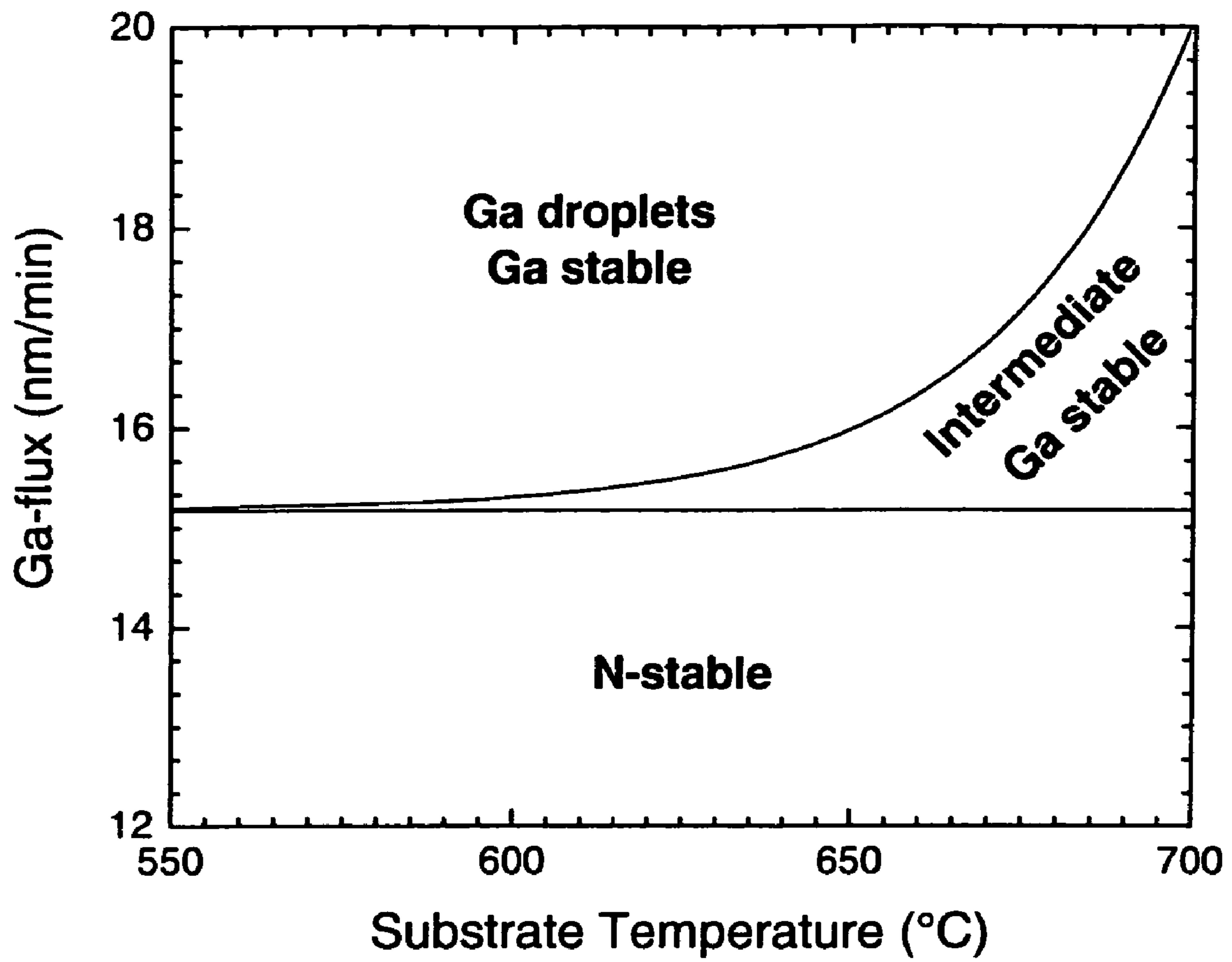


FIG. 3

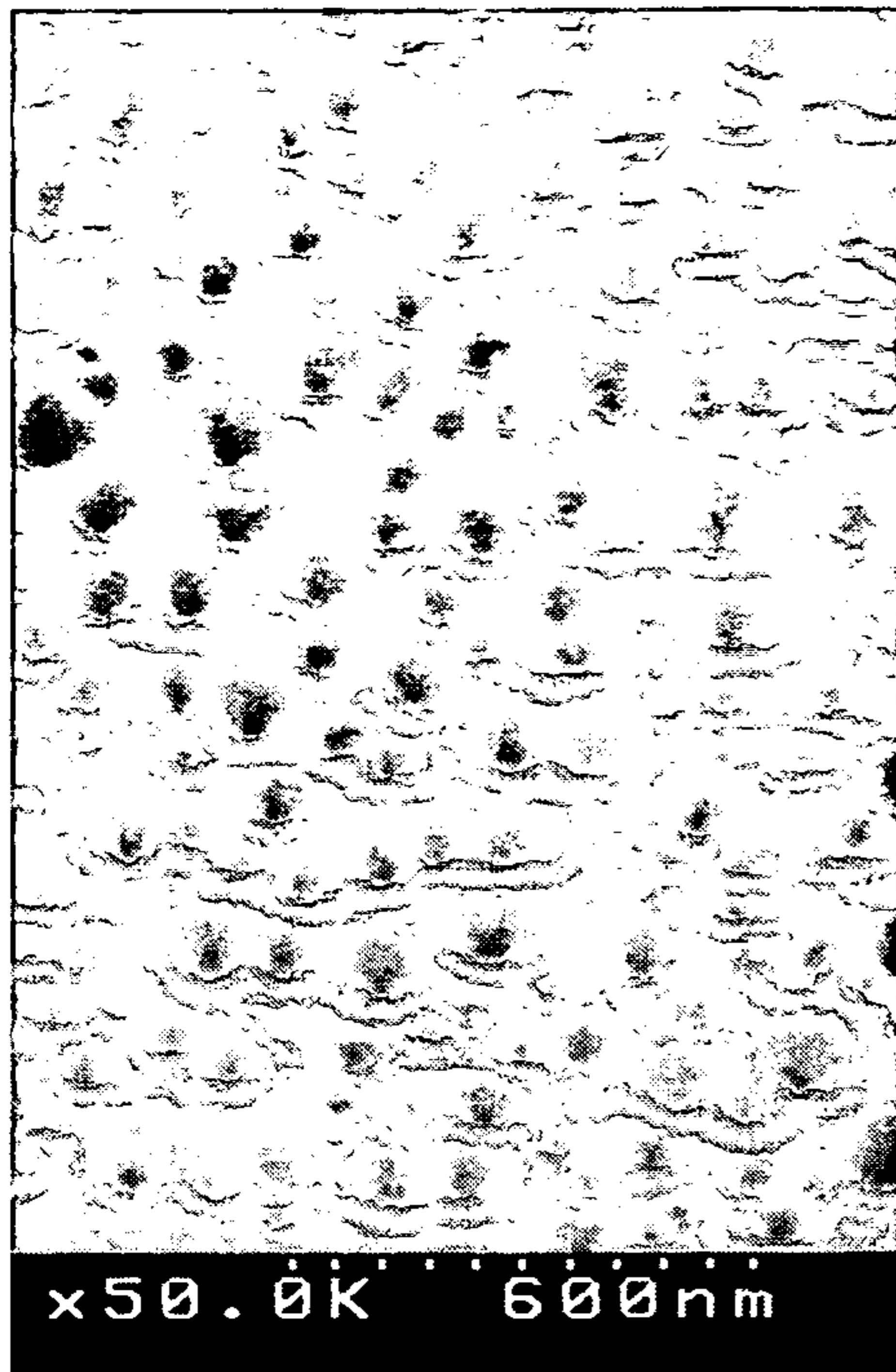


FIG. 4(a)

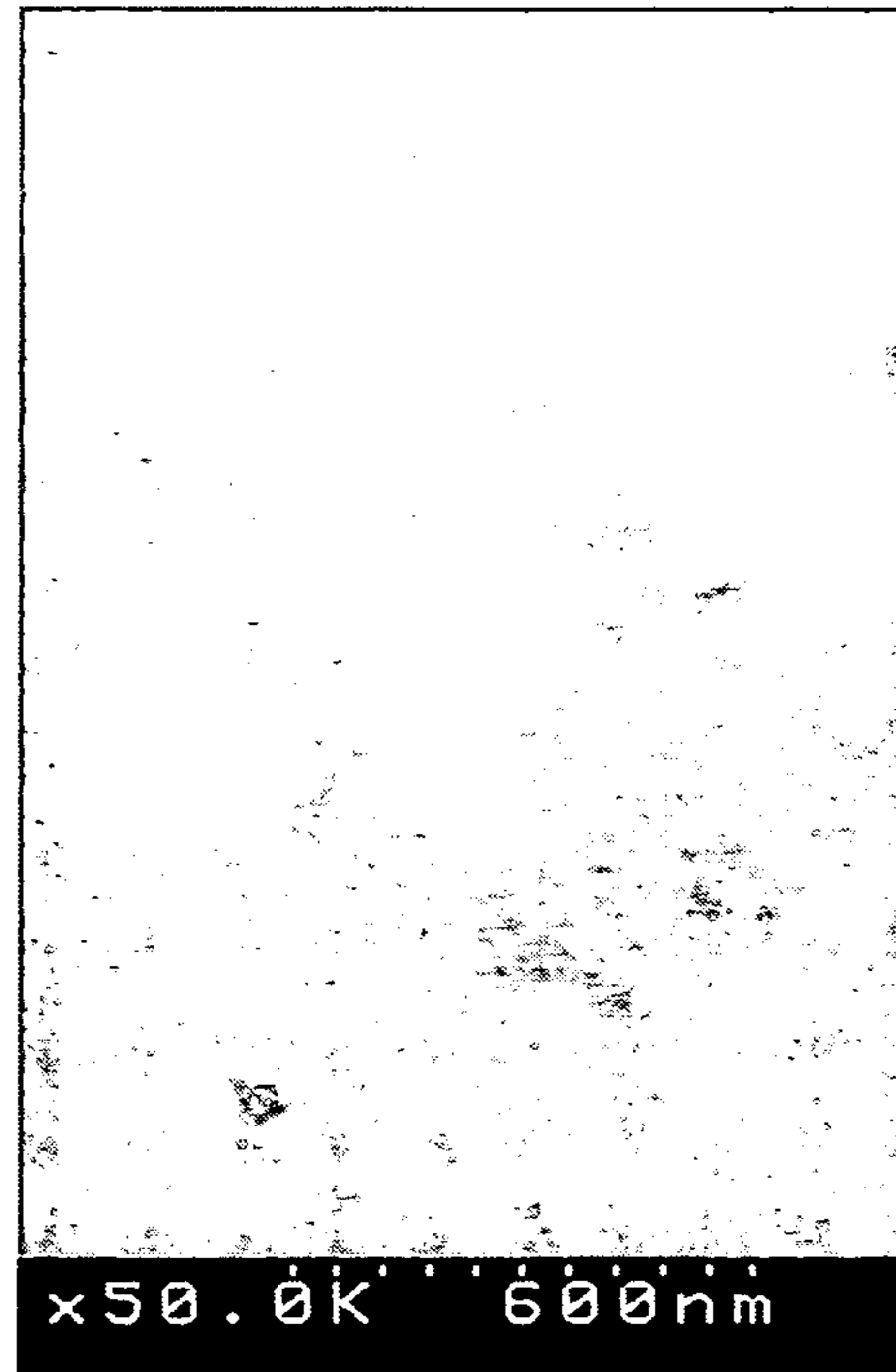


FIG. 4(c)

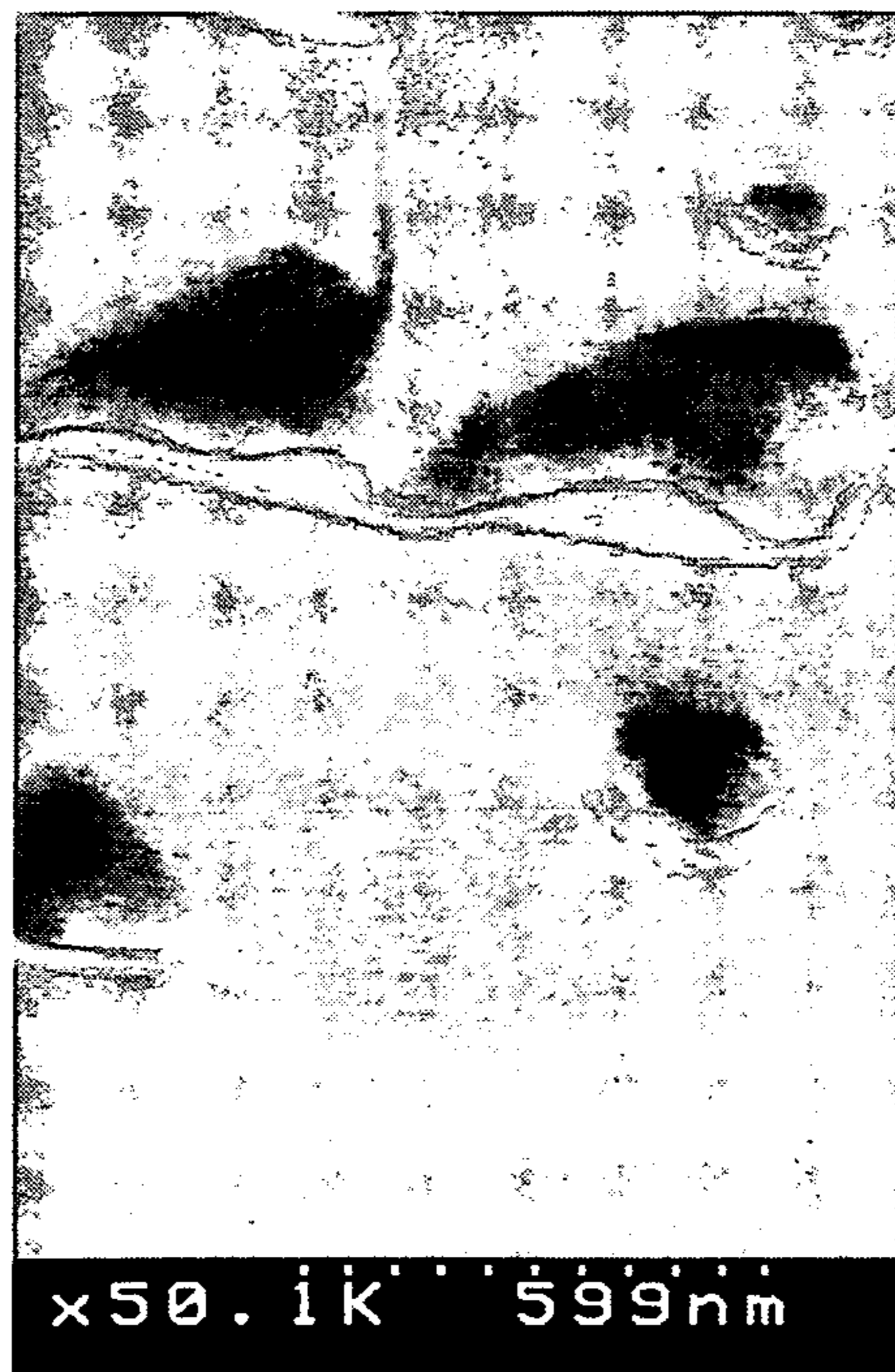


FIG. 4(b)

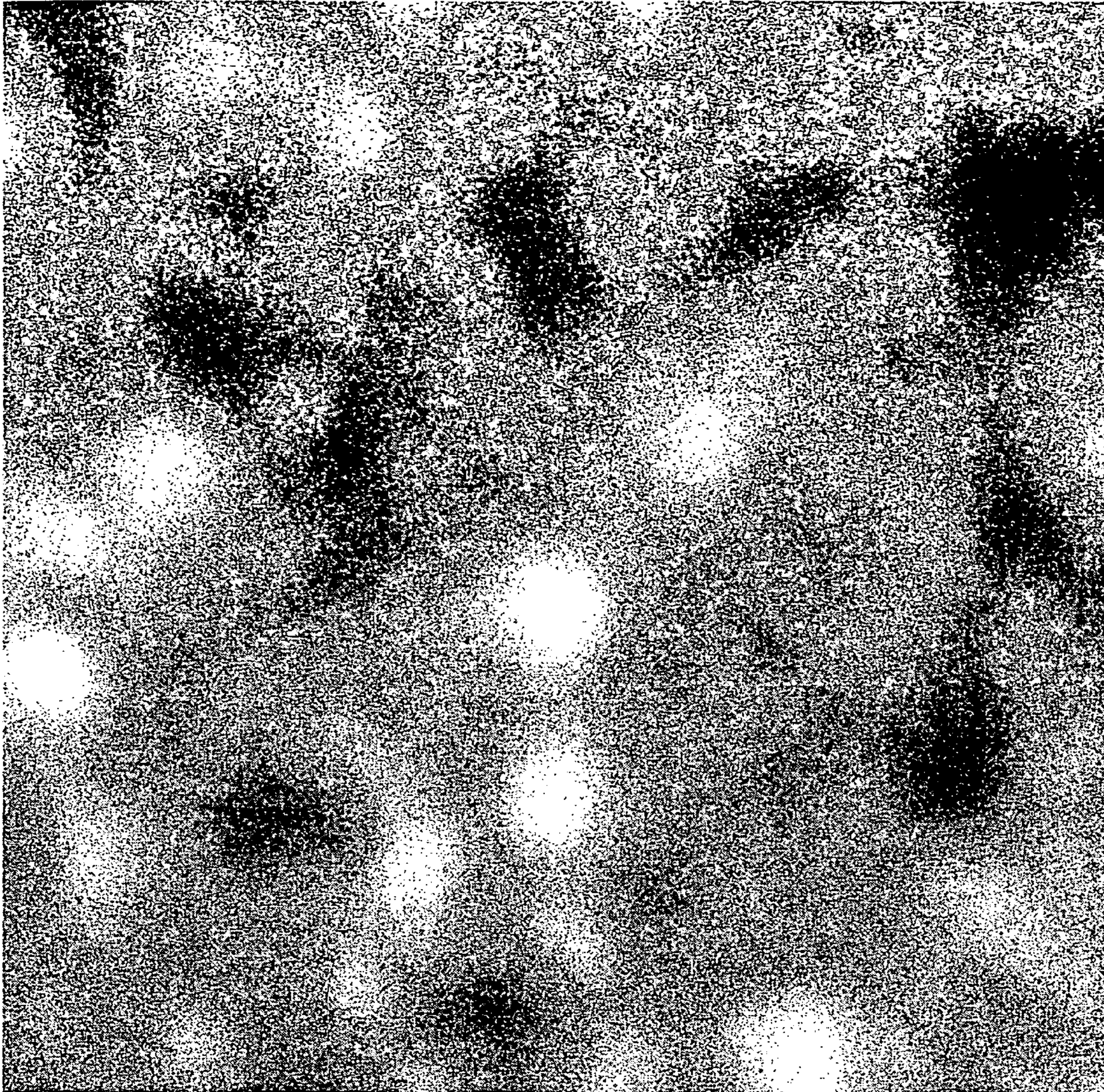


FIG. 5

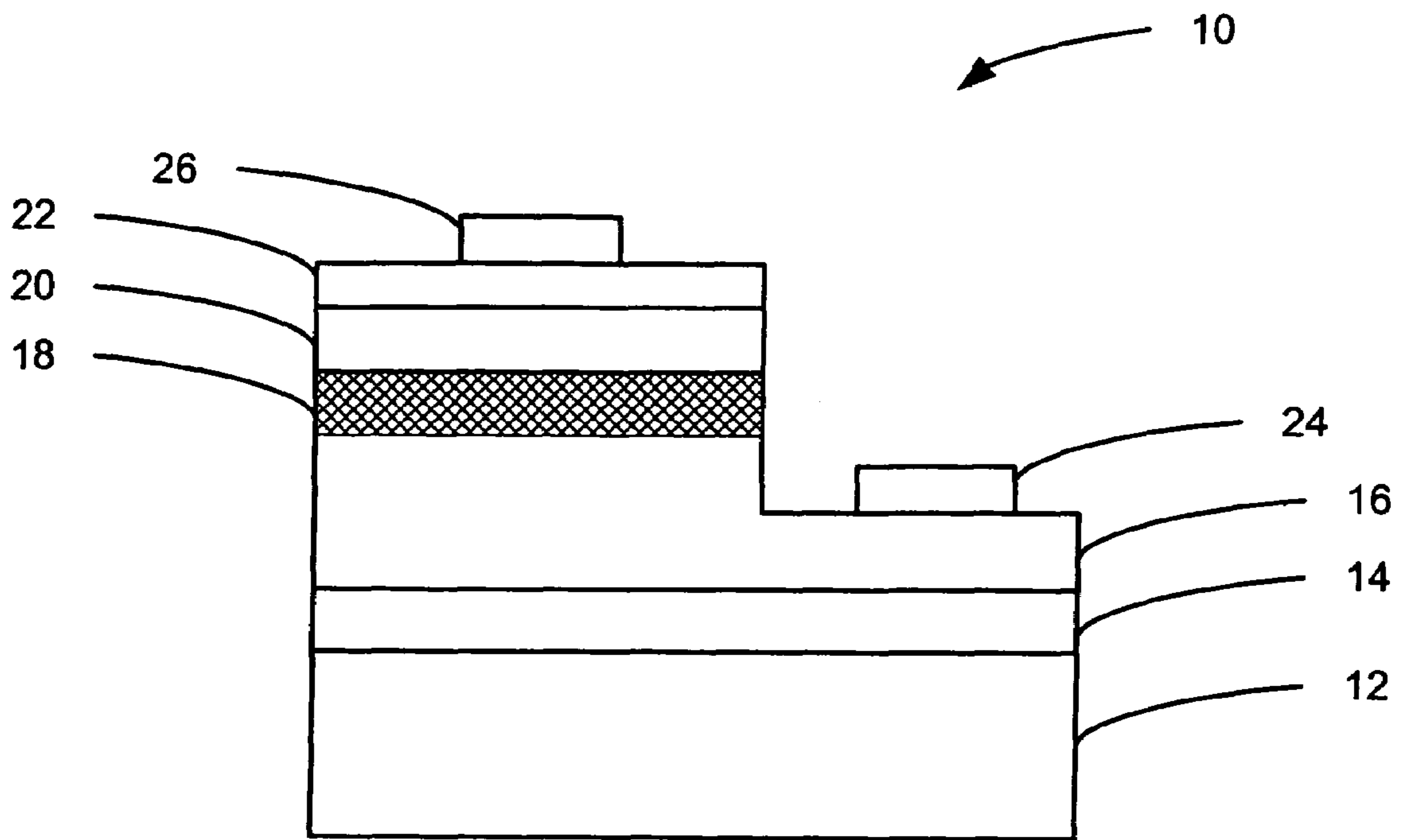


FIG. 6



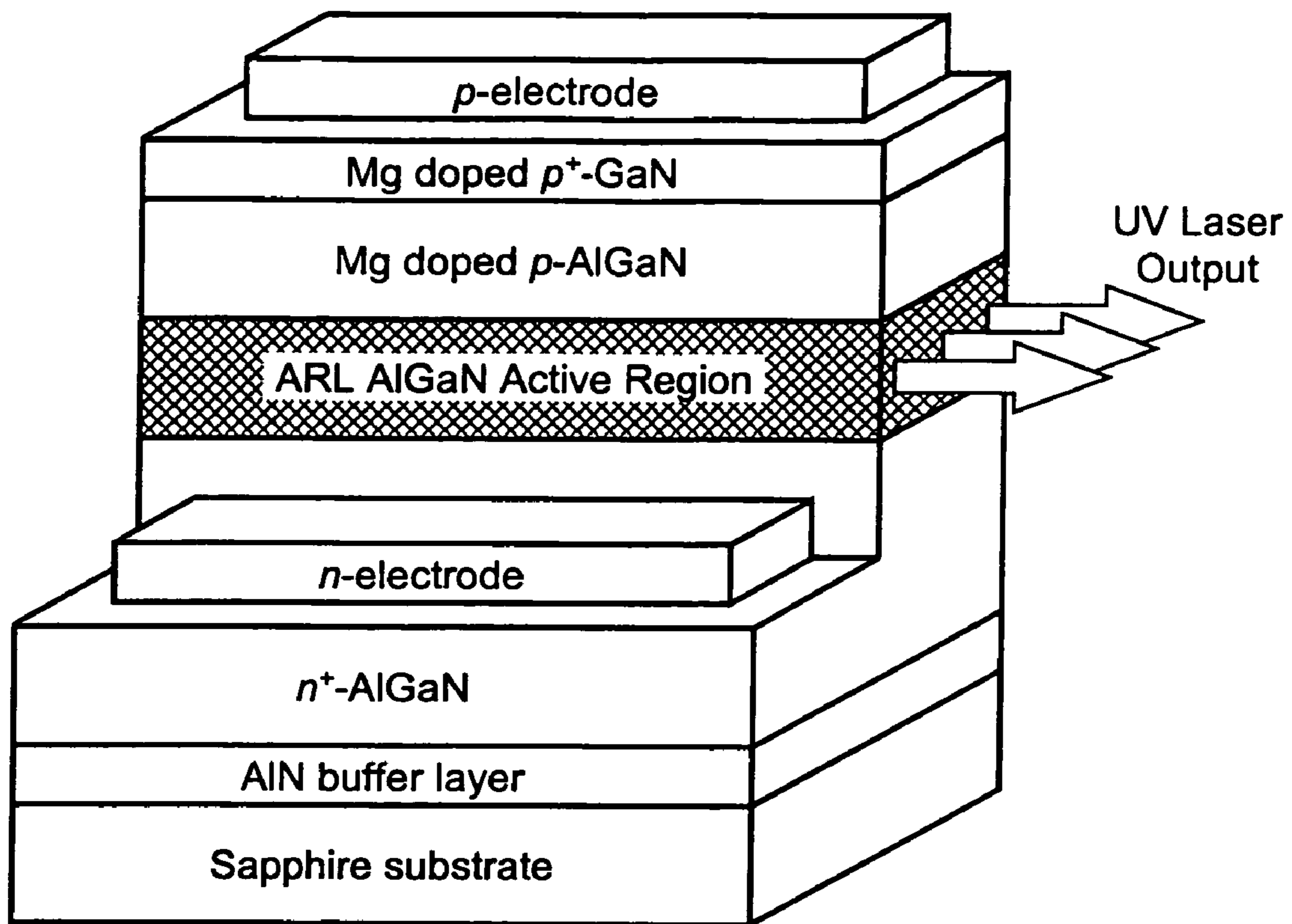


FIG. 7(a)

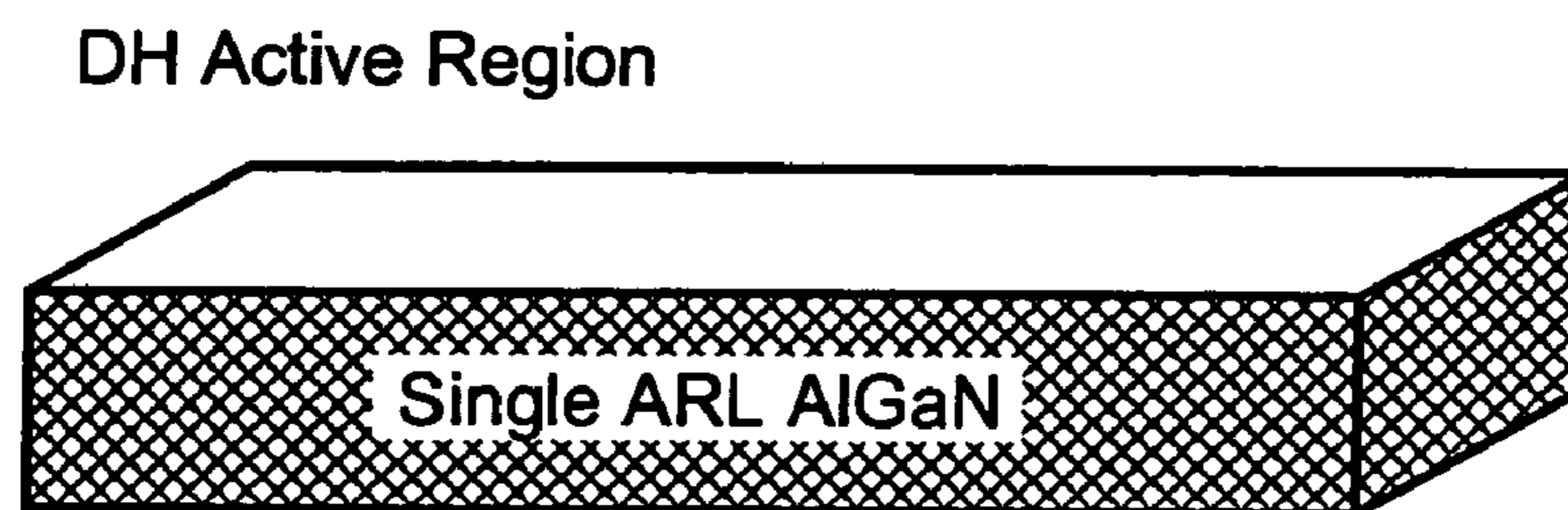


FIG. 7(b)

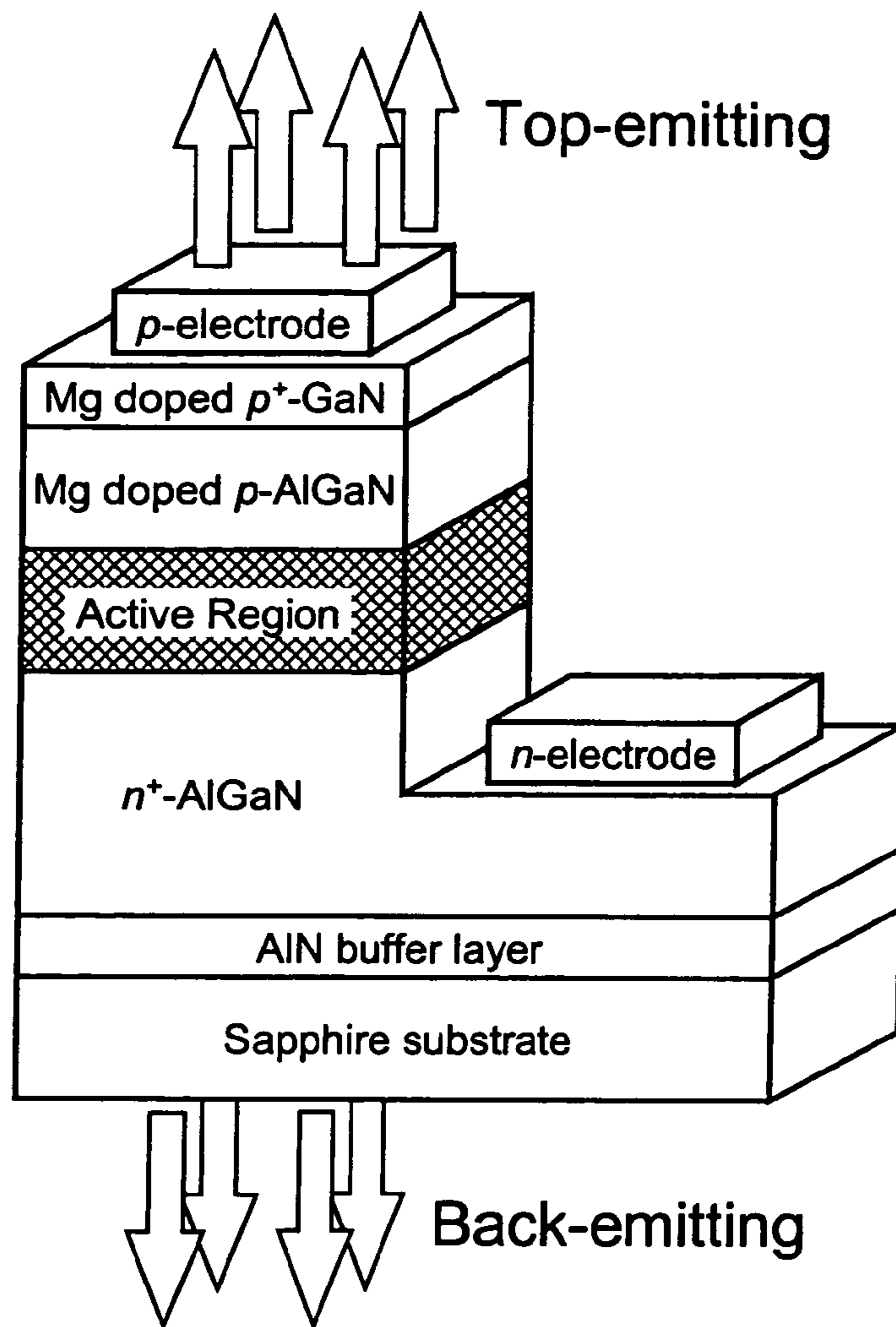


FIG. 8(a)

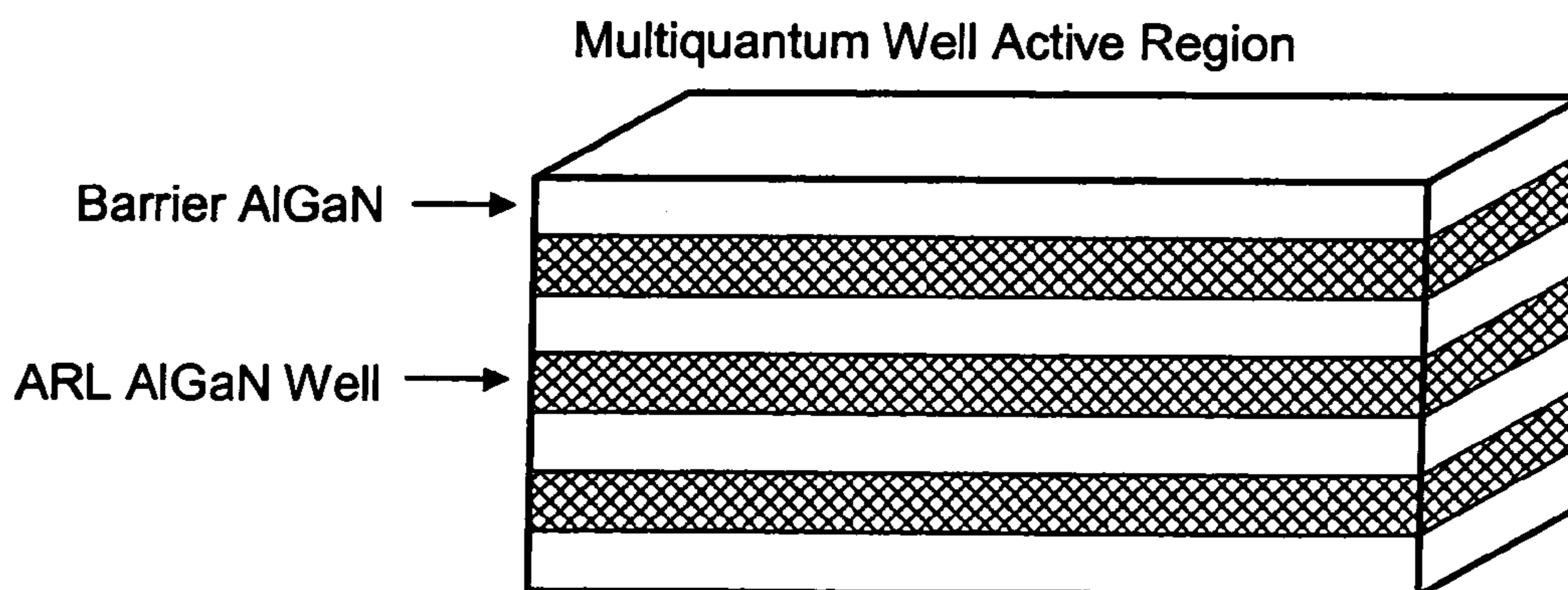


FIG. 8(b)

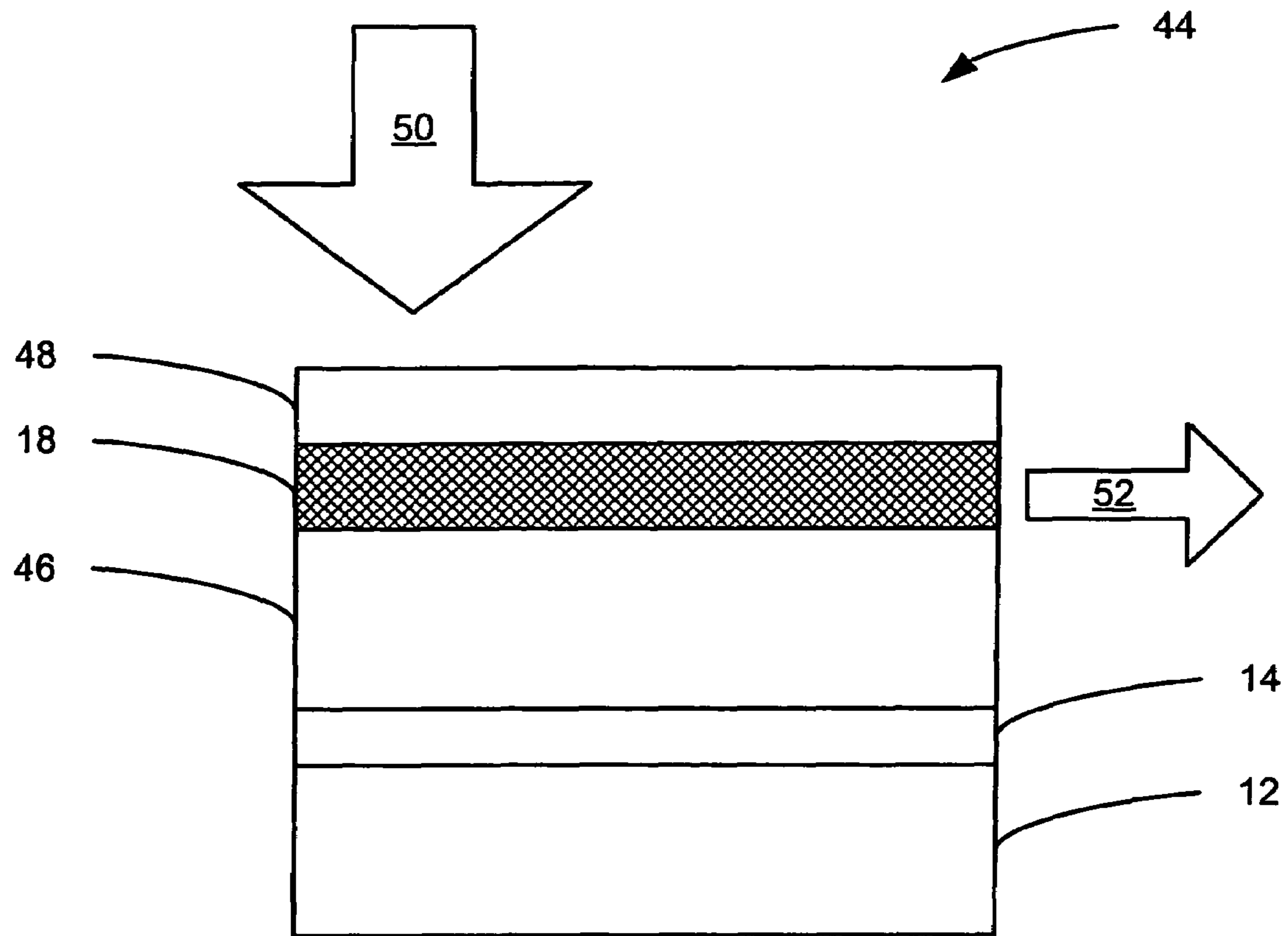


FIG. 9

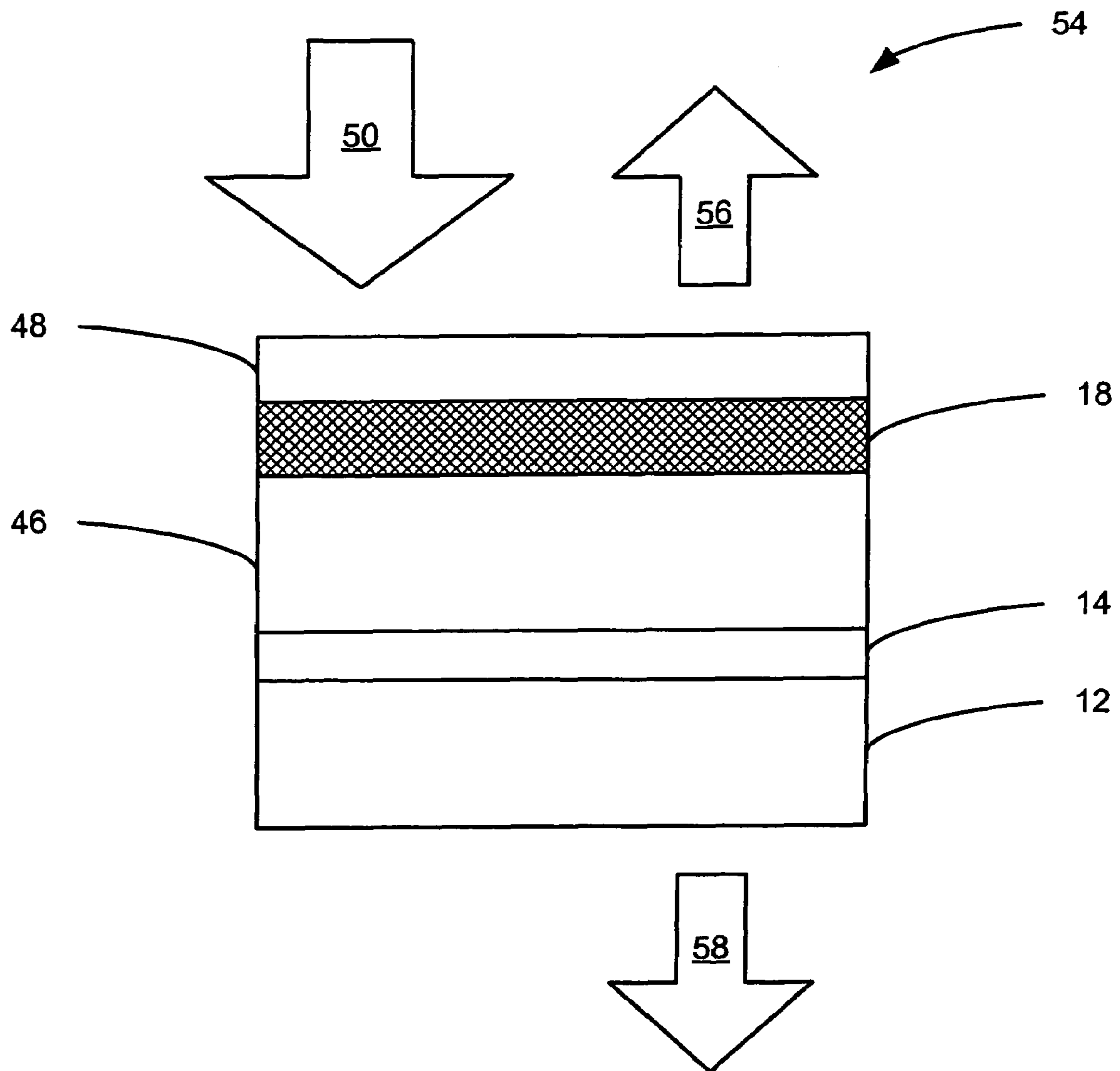


FIG. 10

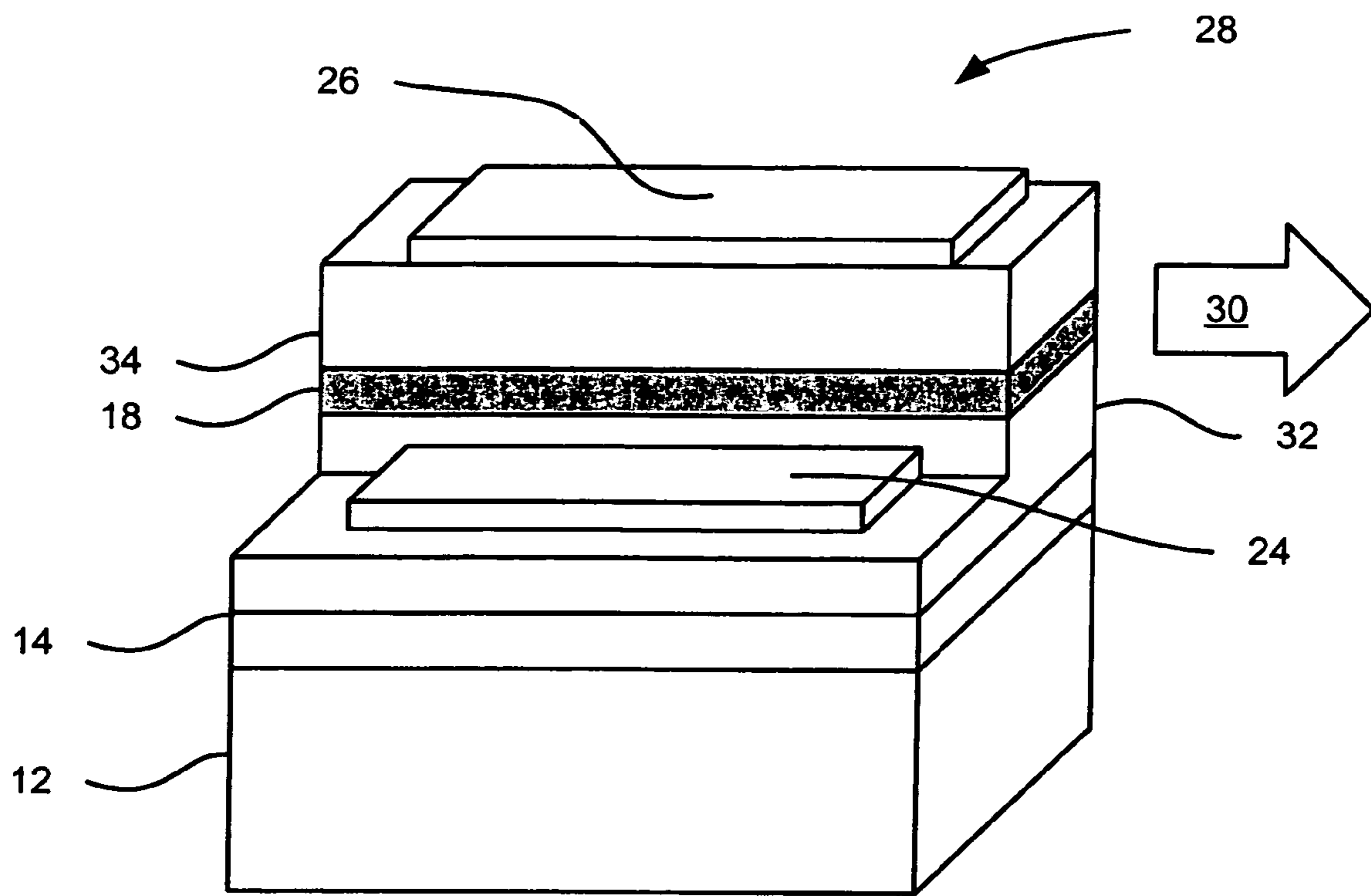


FIG. 11

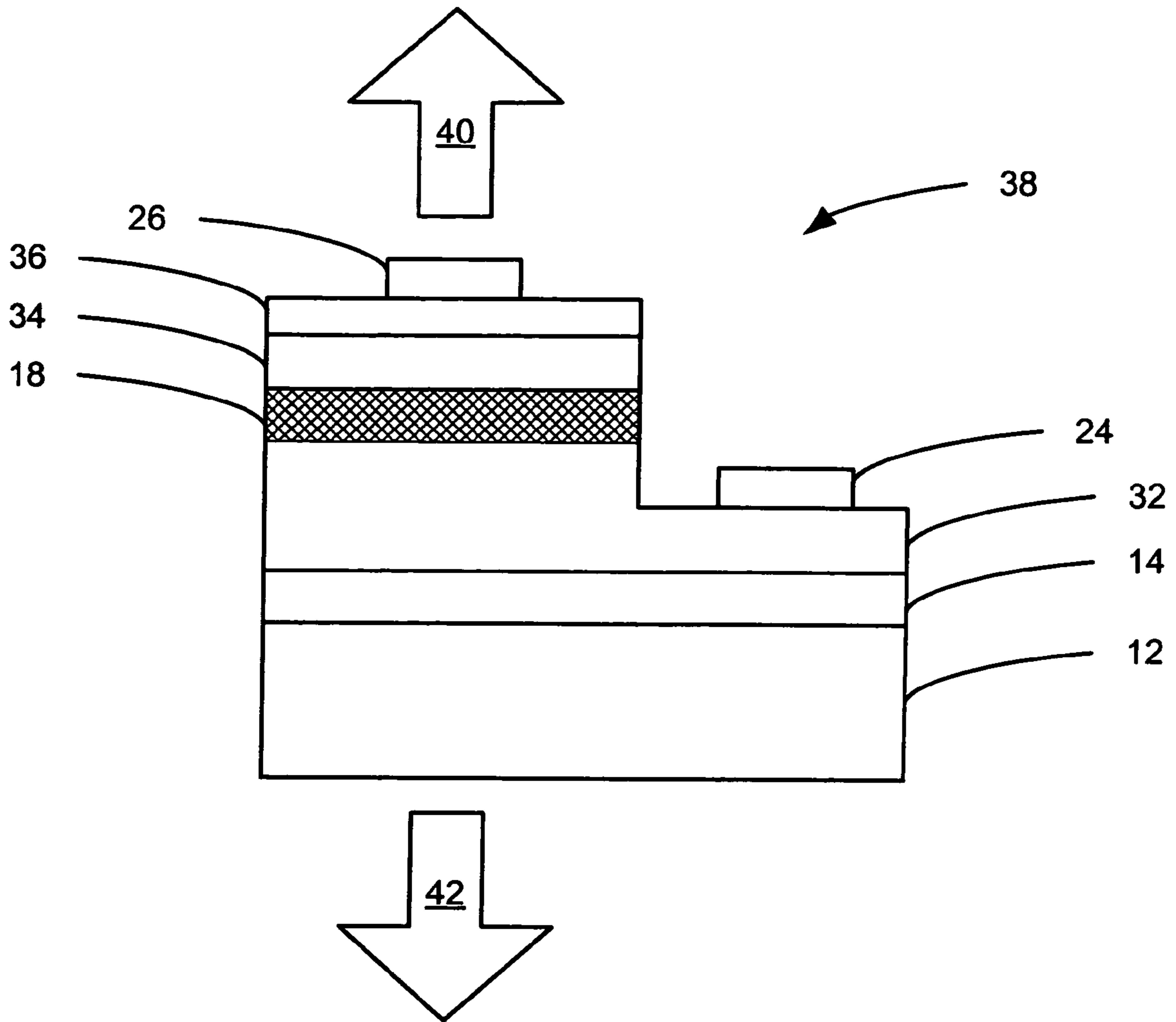


FIG. 12

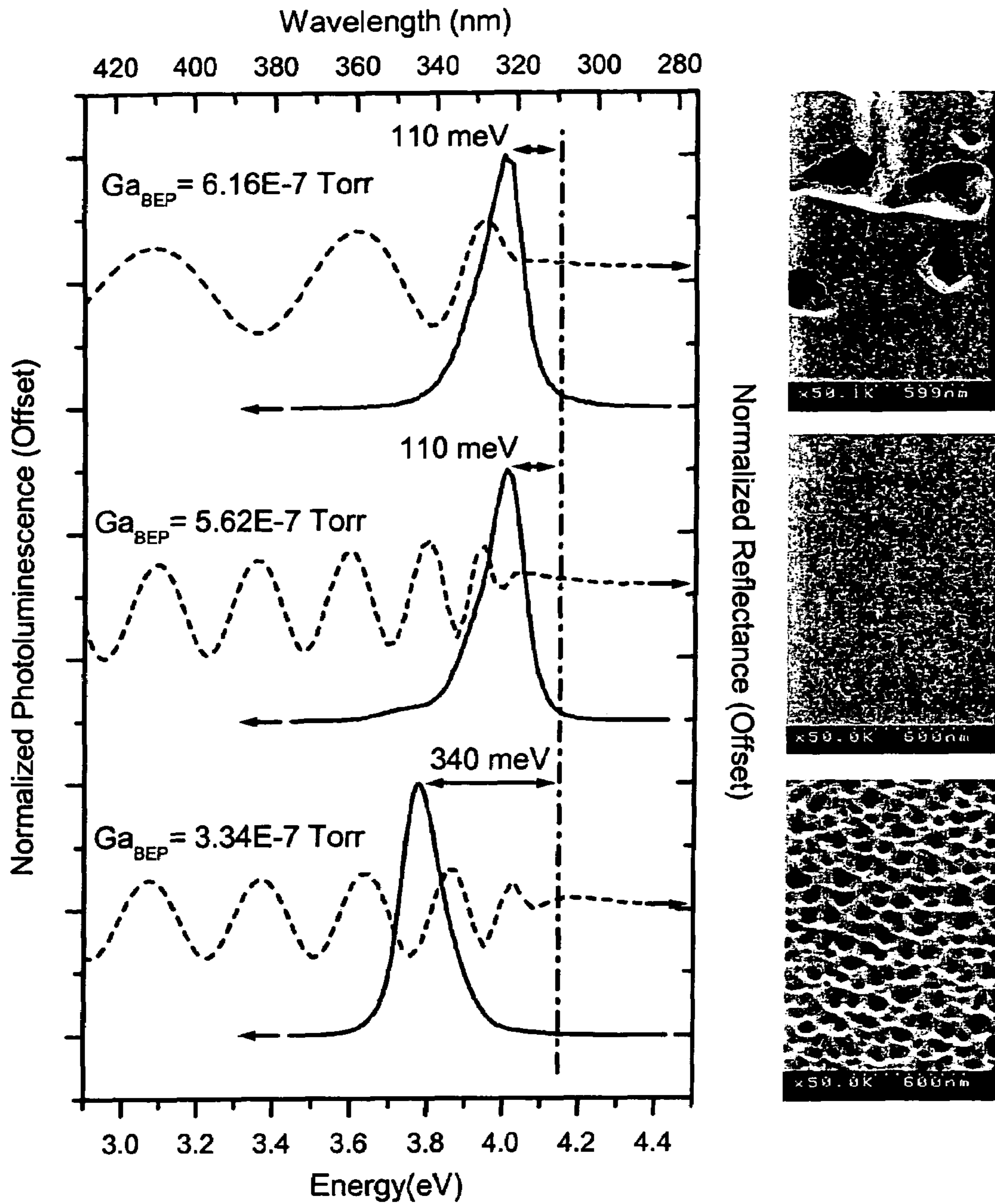


FIG. 13

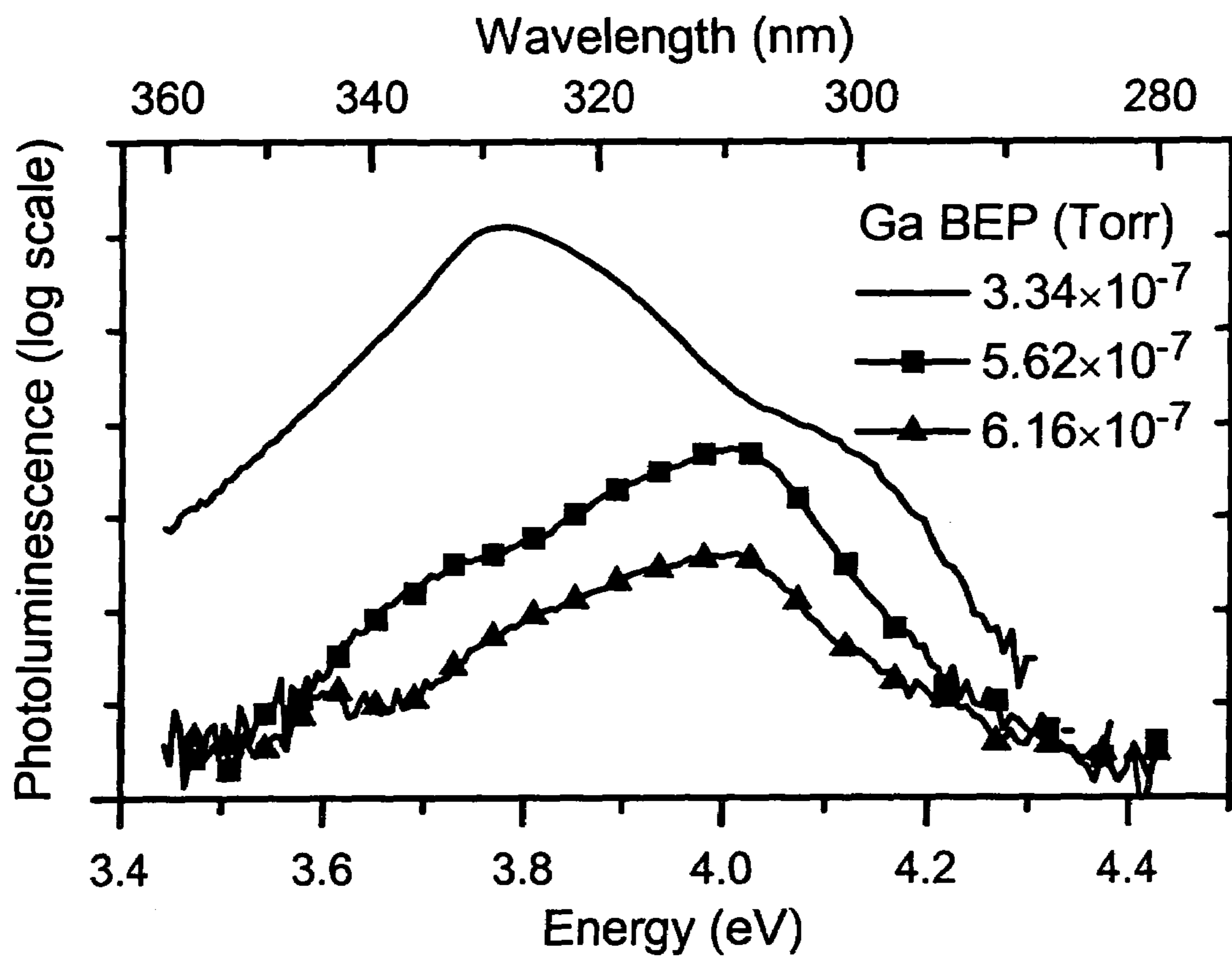


FIG. 14



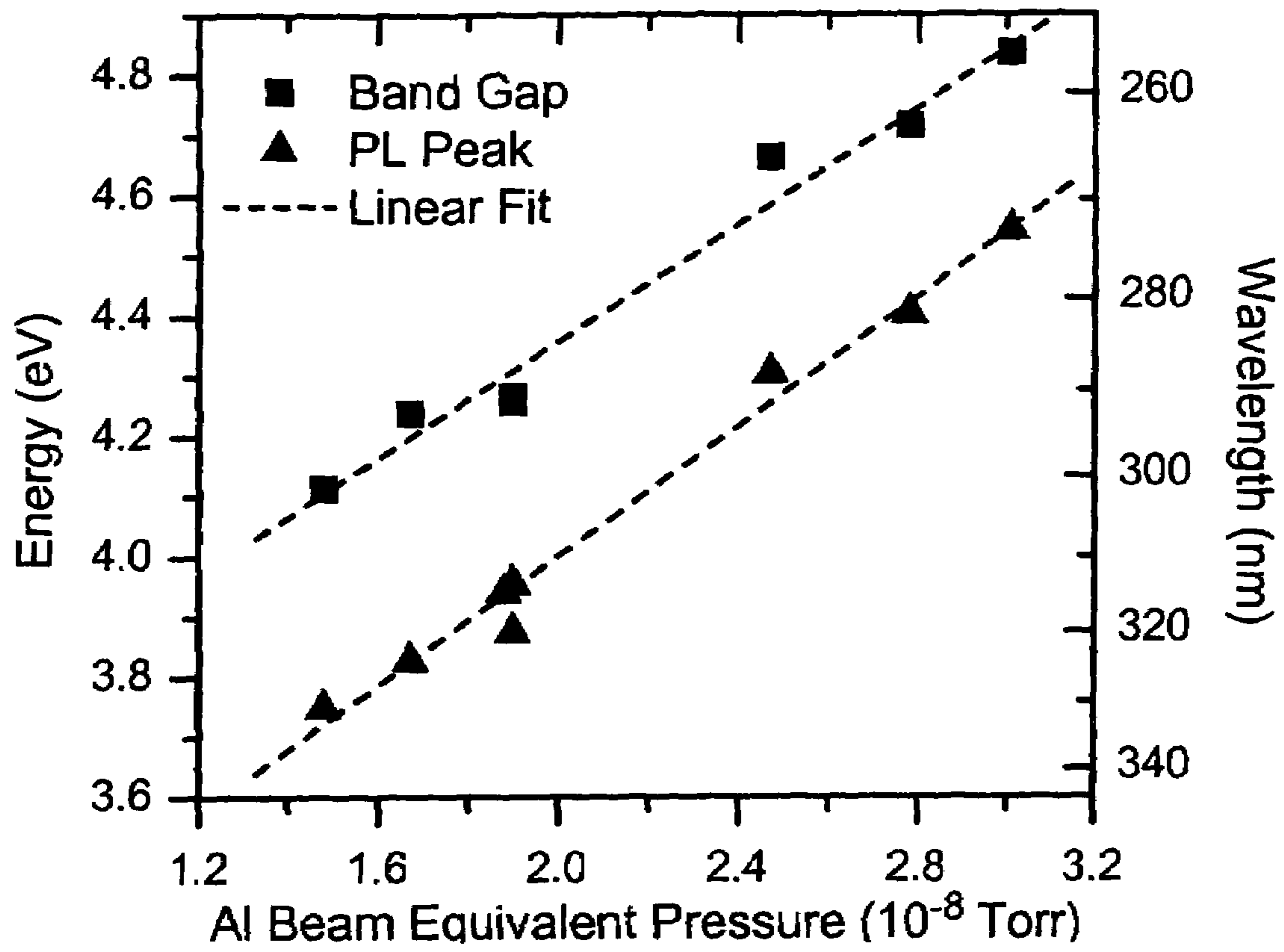


FIG. 15

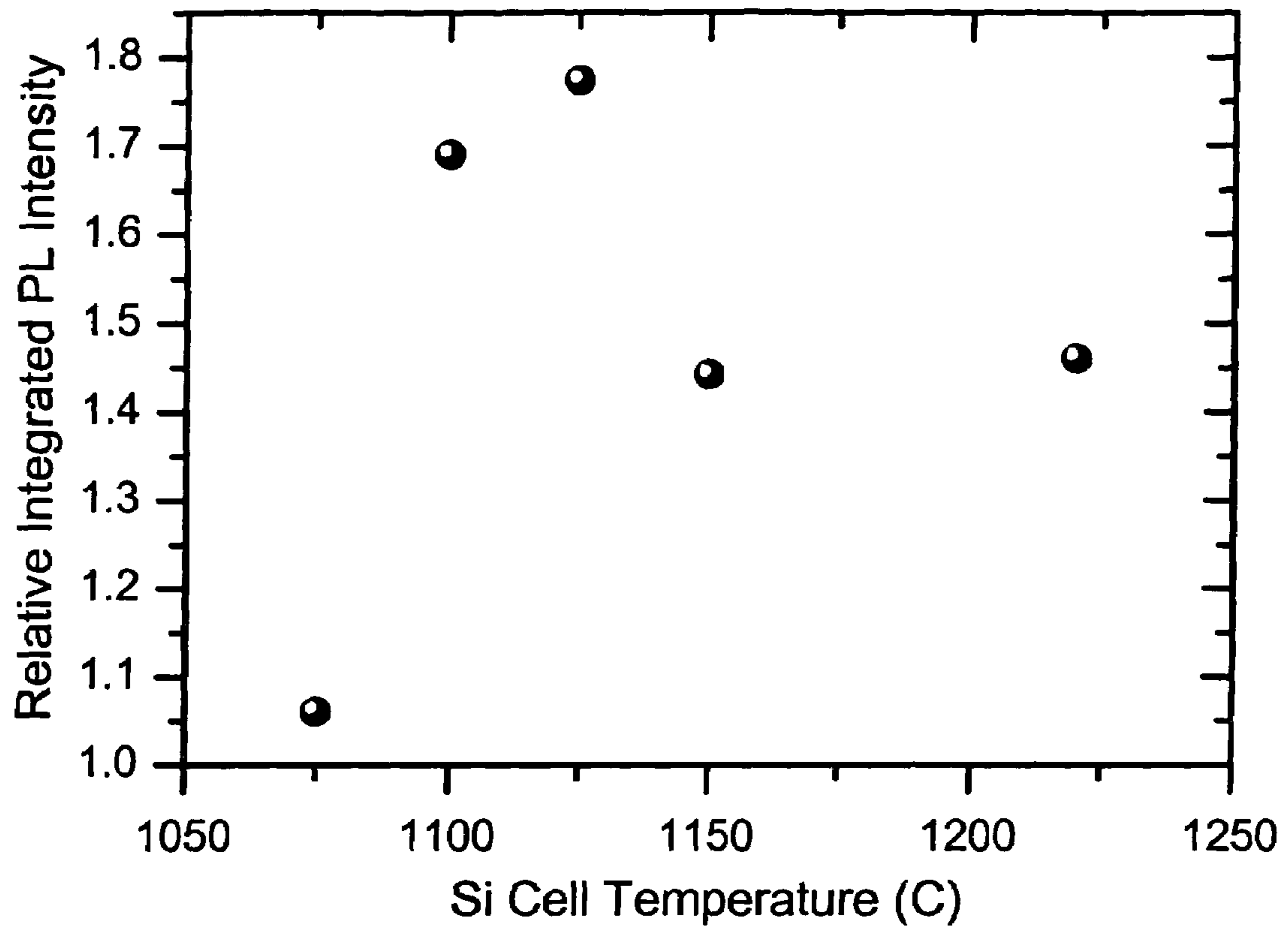


FIG. 16

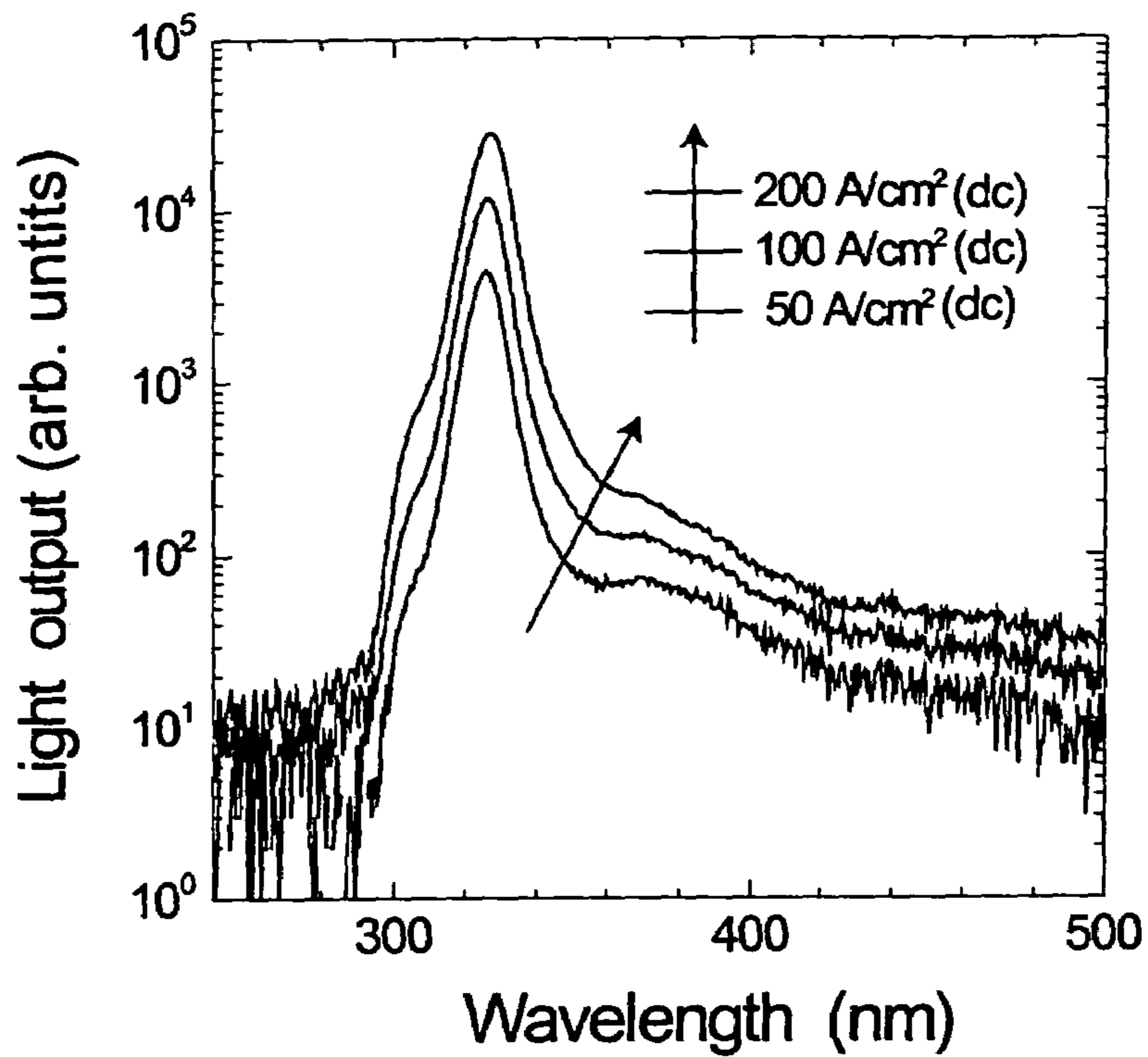


FIG. 17(a)

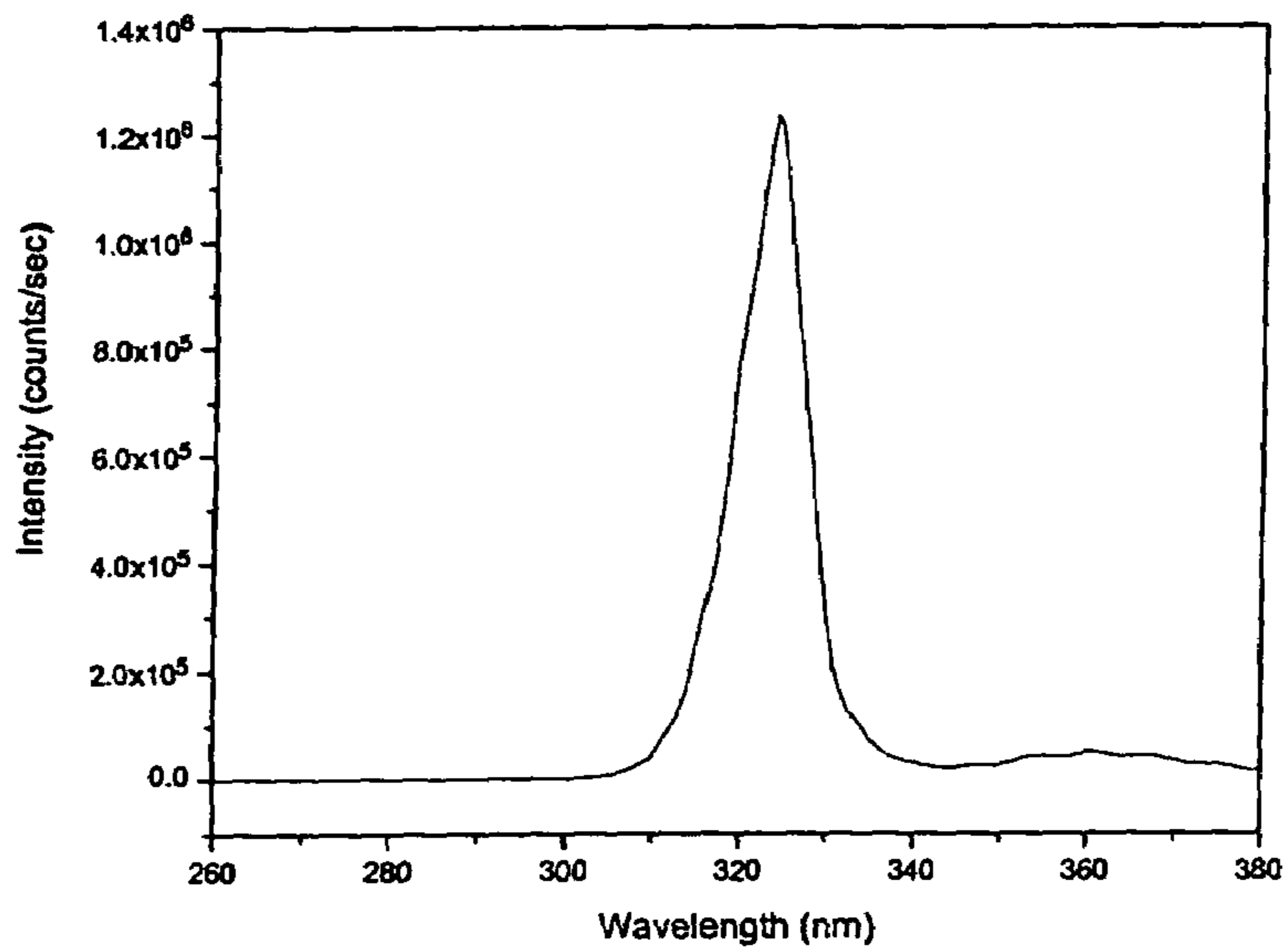


FIG. 17 (b)

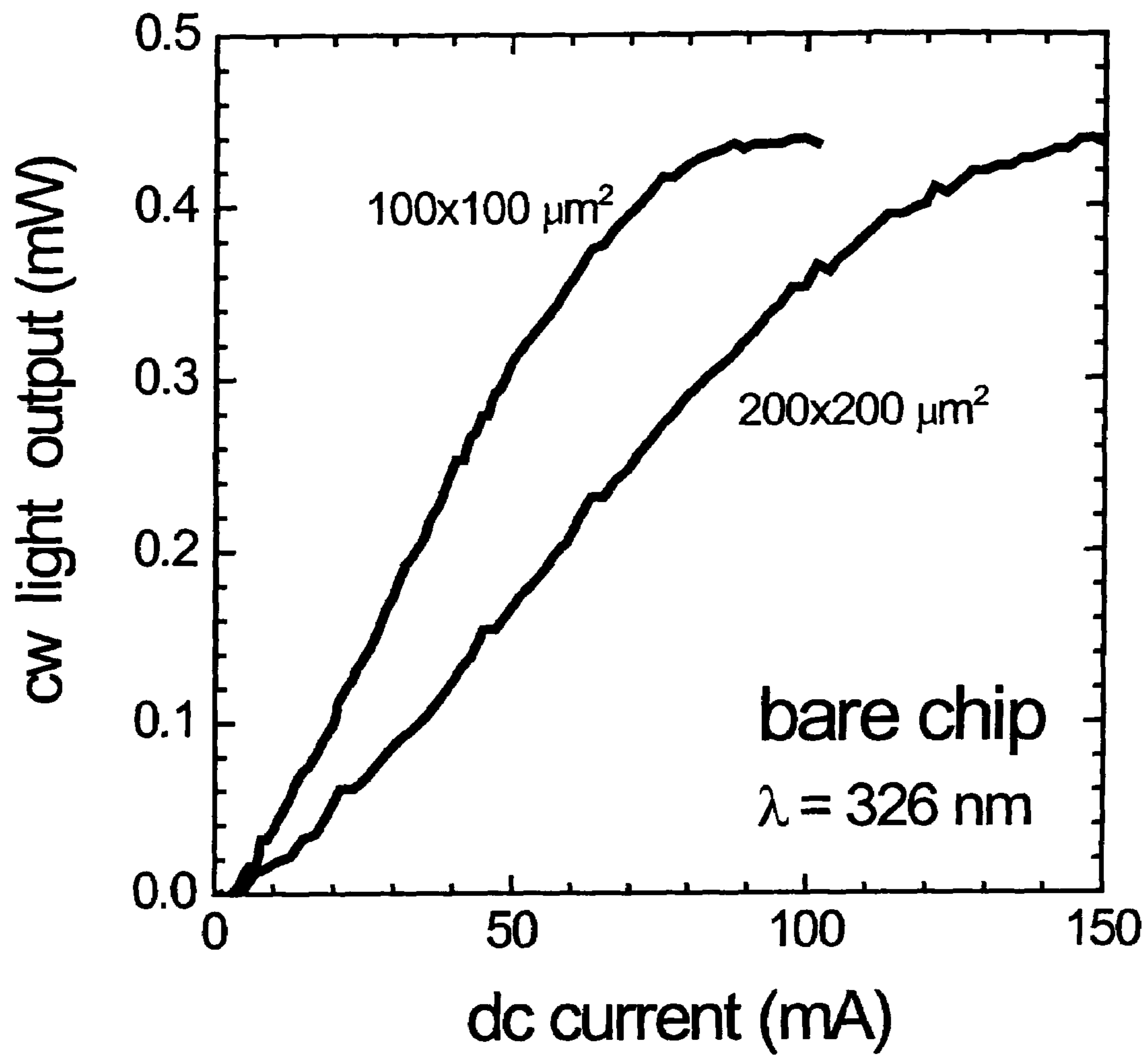


FIG. 18

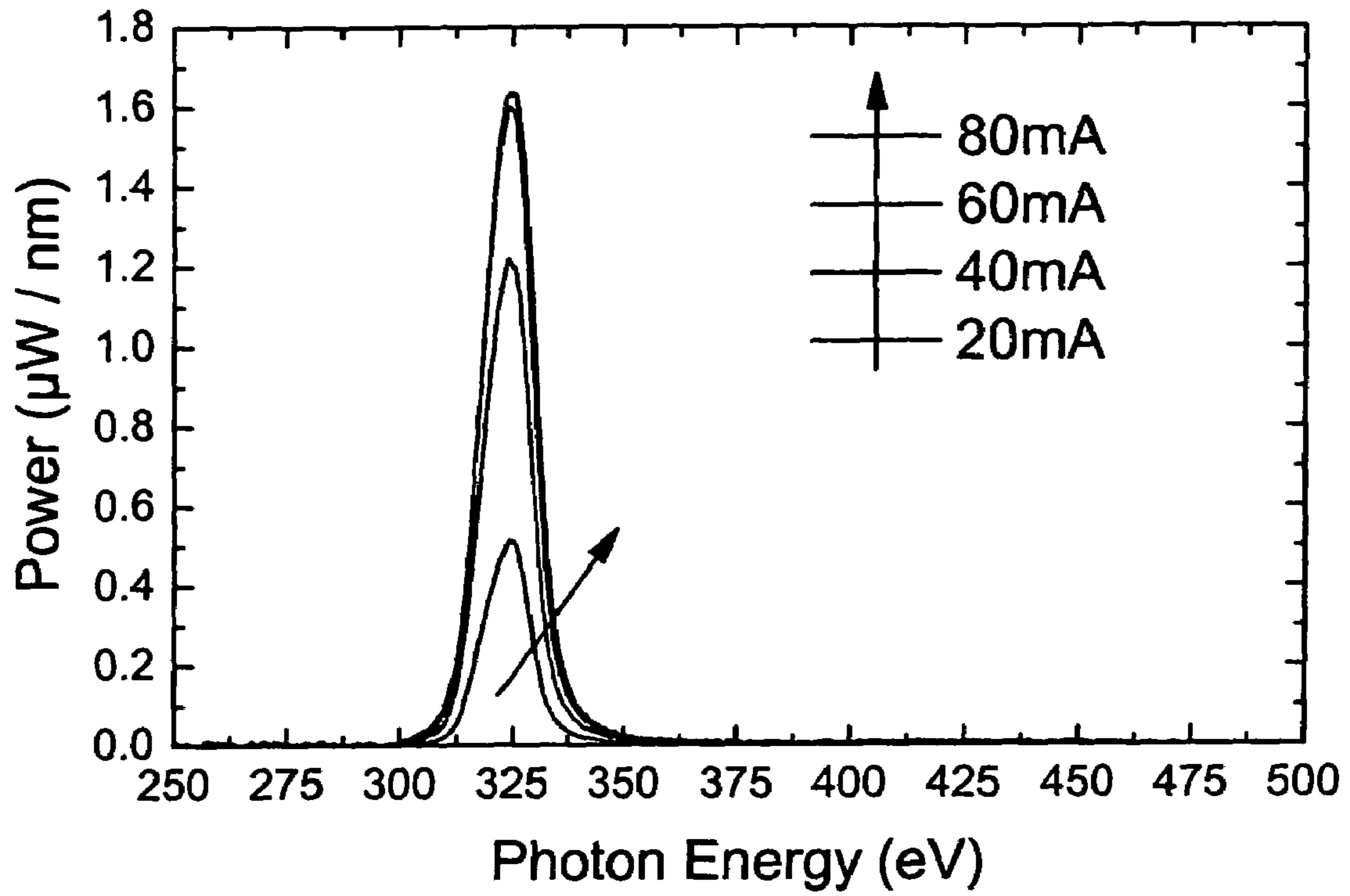


FIG. 19

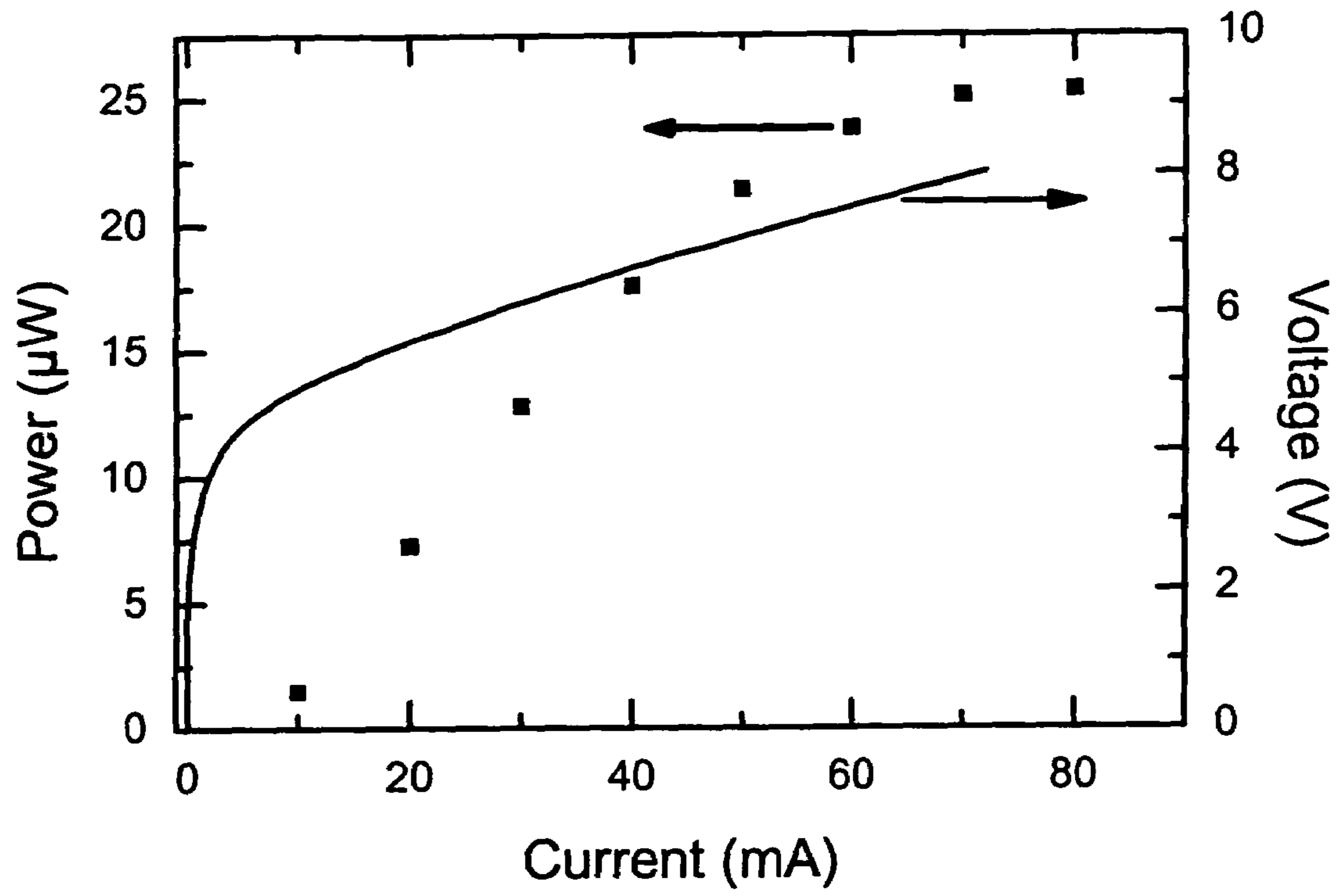


FIG. 20

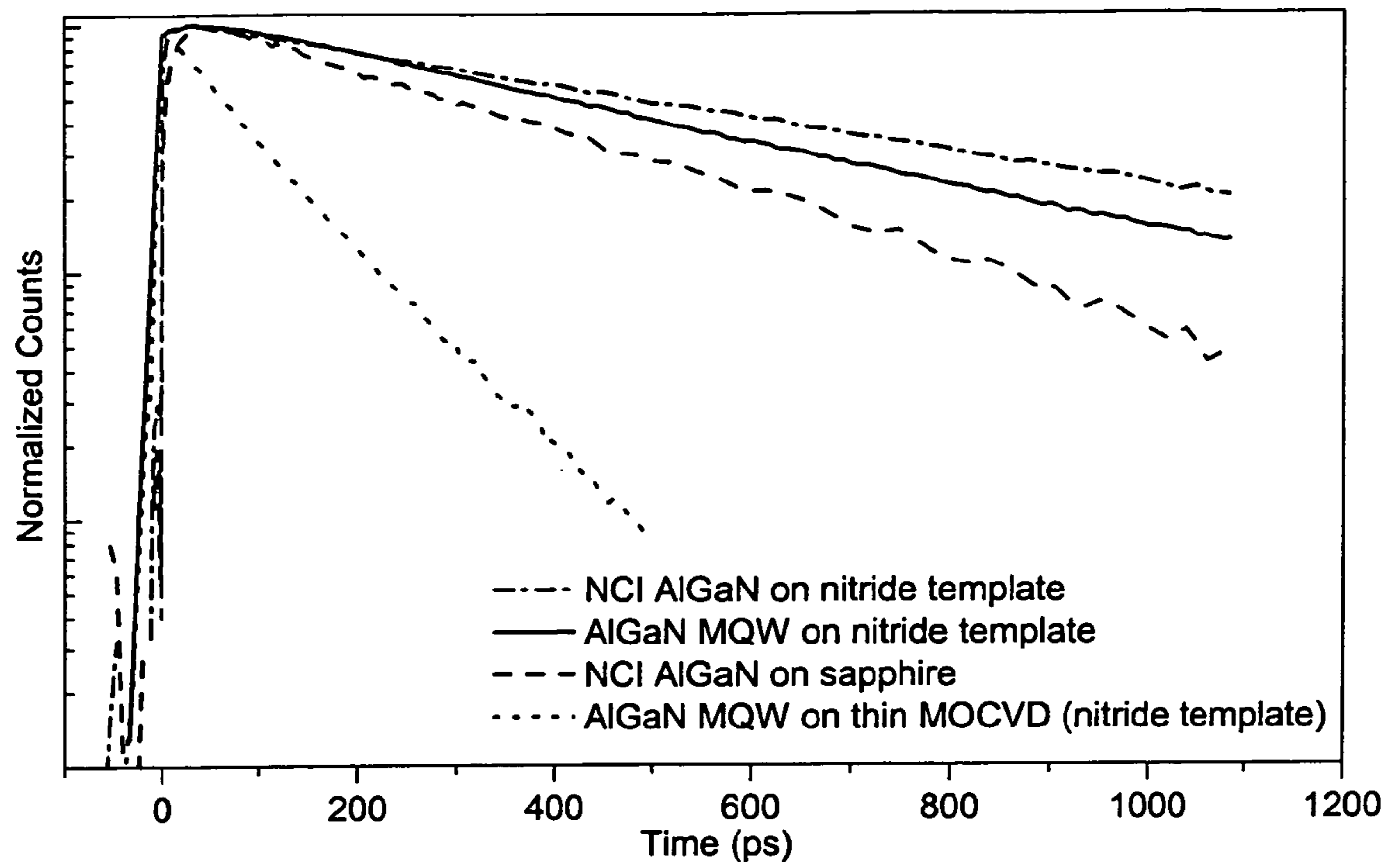


FIG. 21

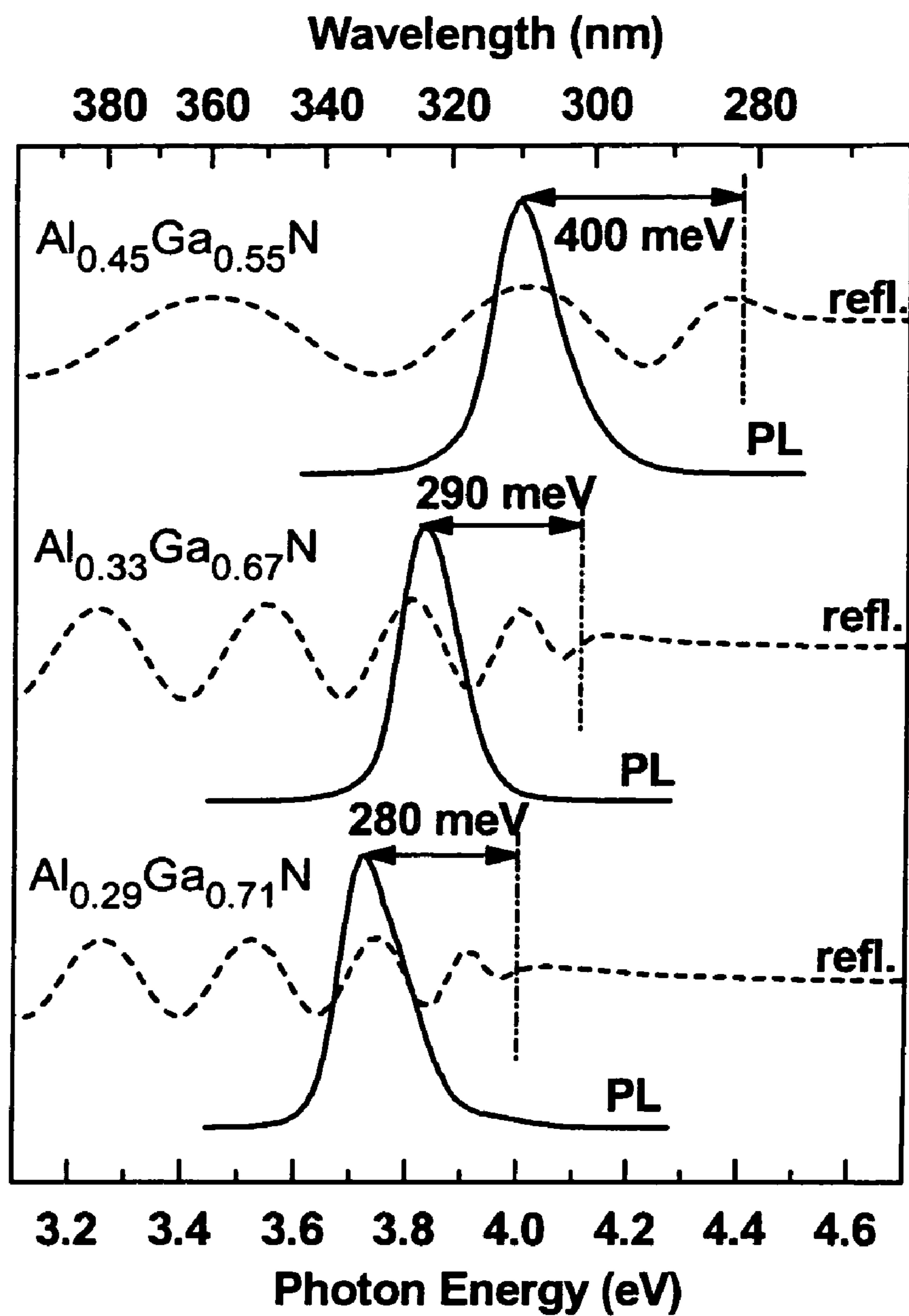


FIG. 22



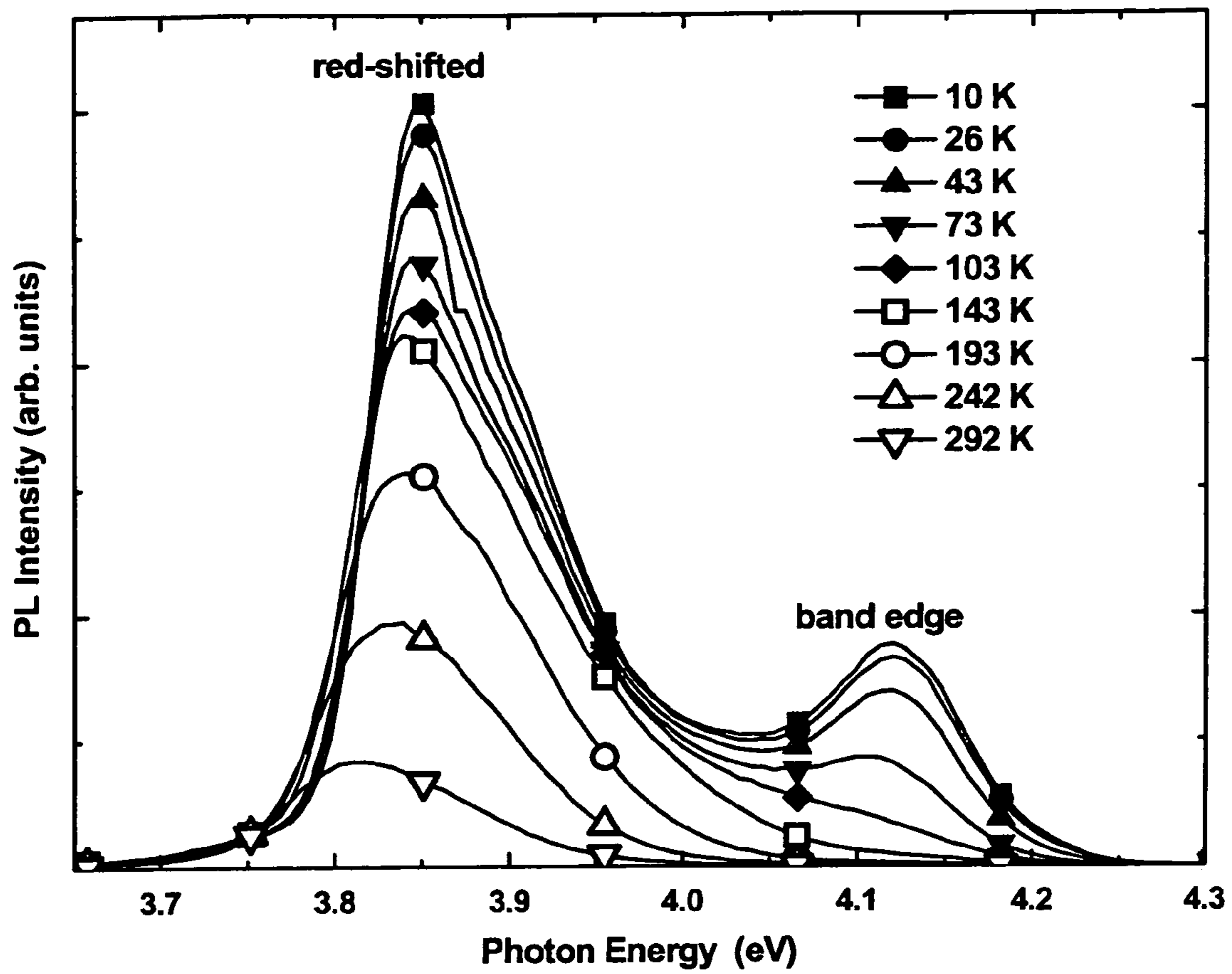


FIG. 23

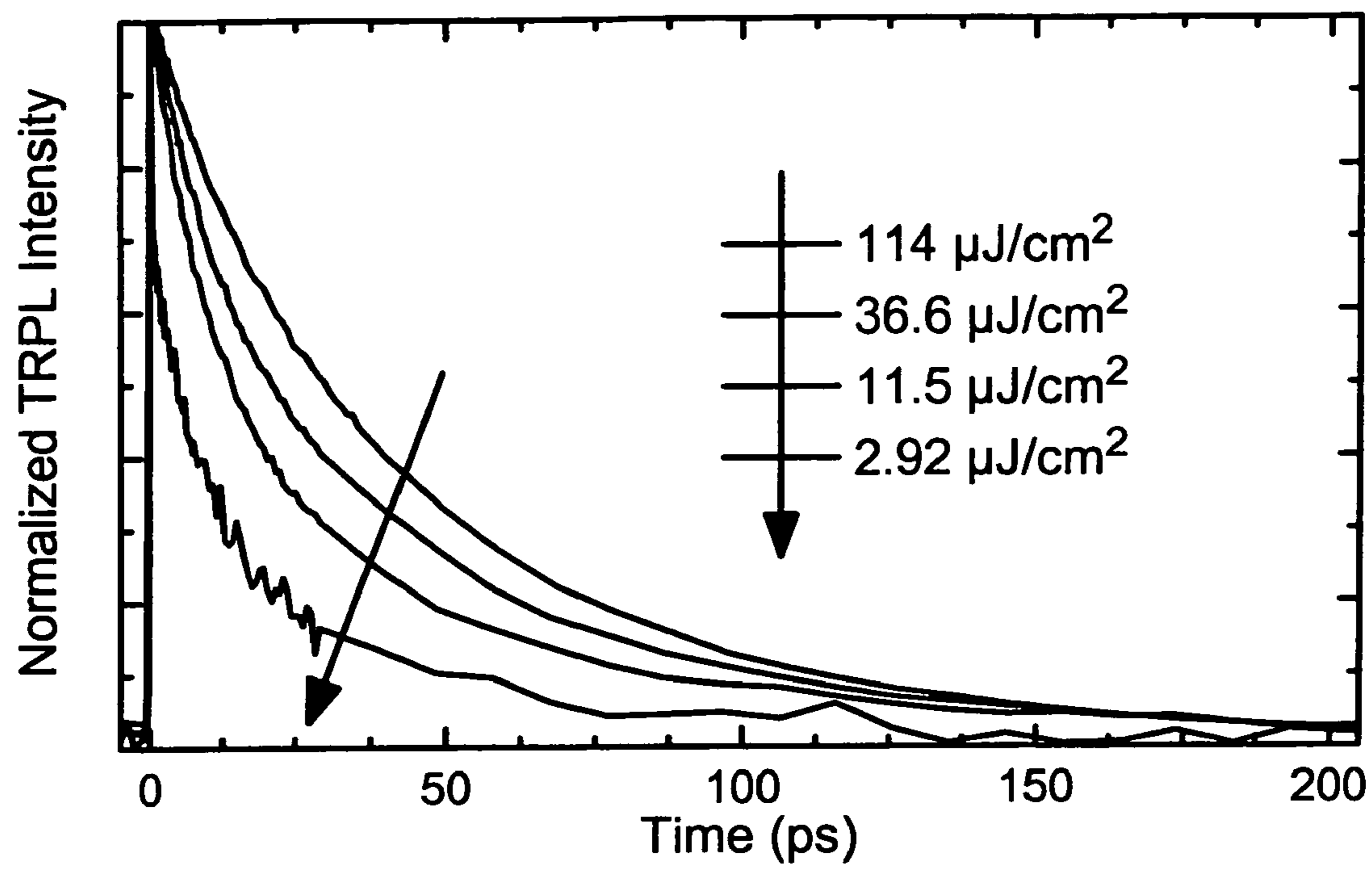


FIG. 24

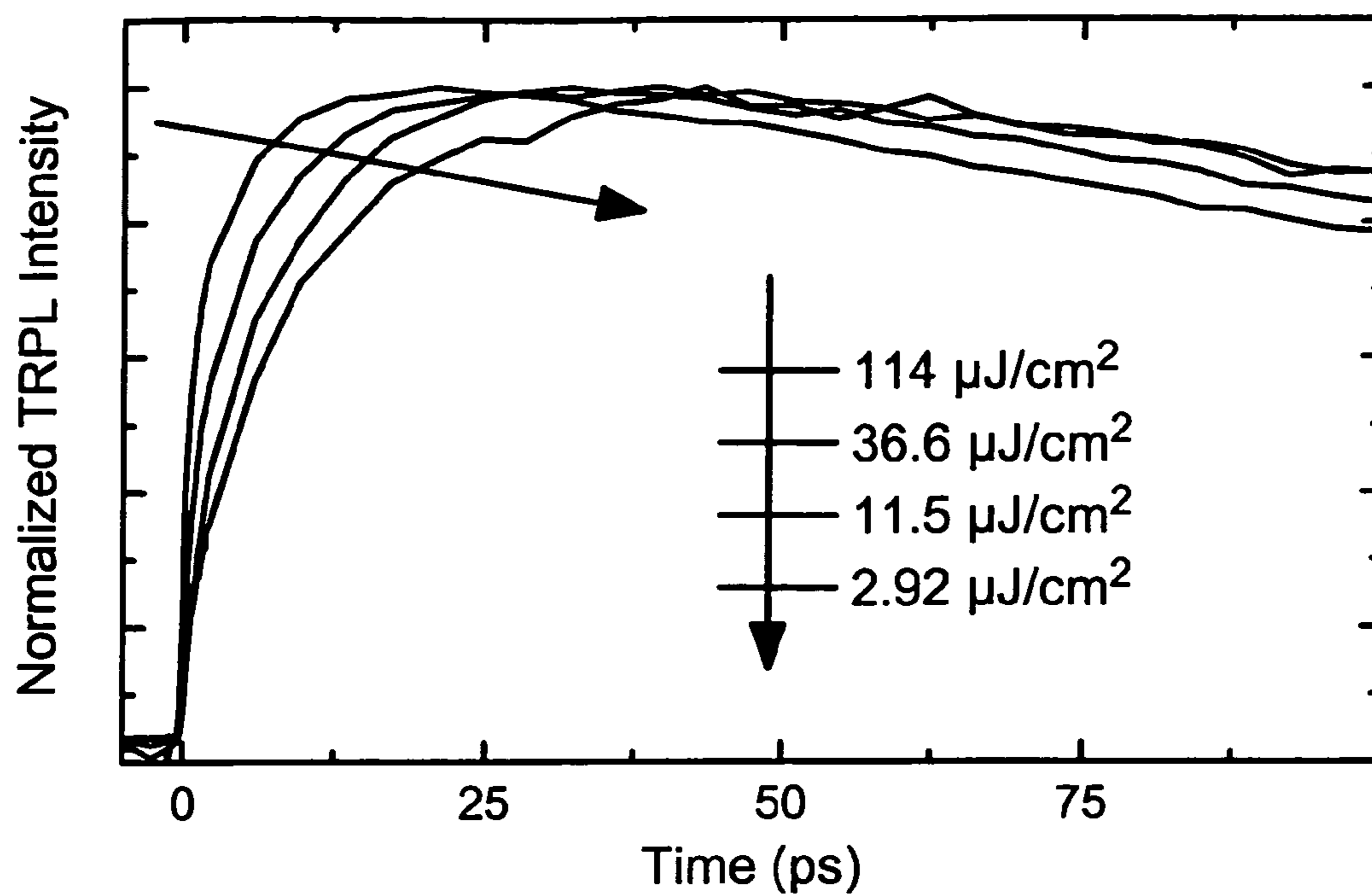


FIG. 25

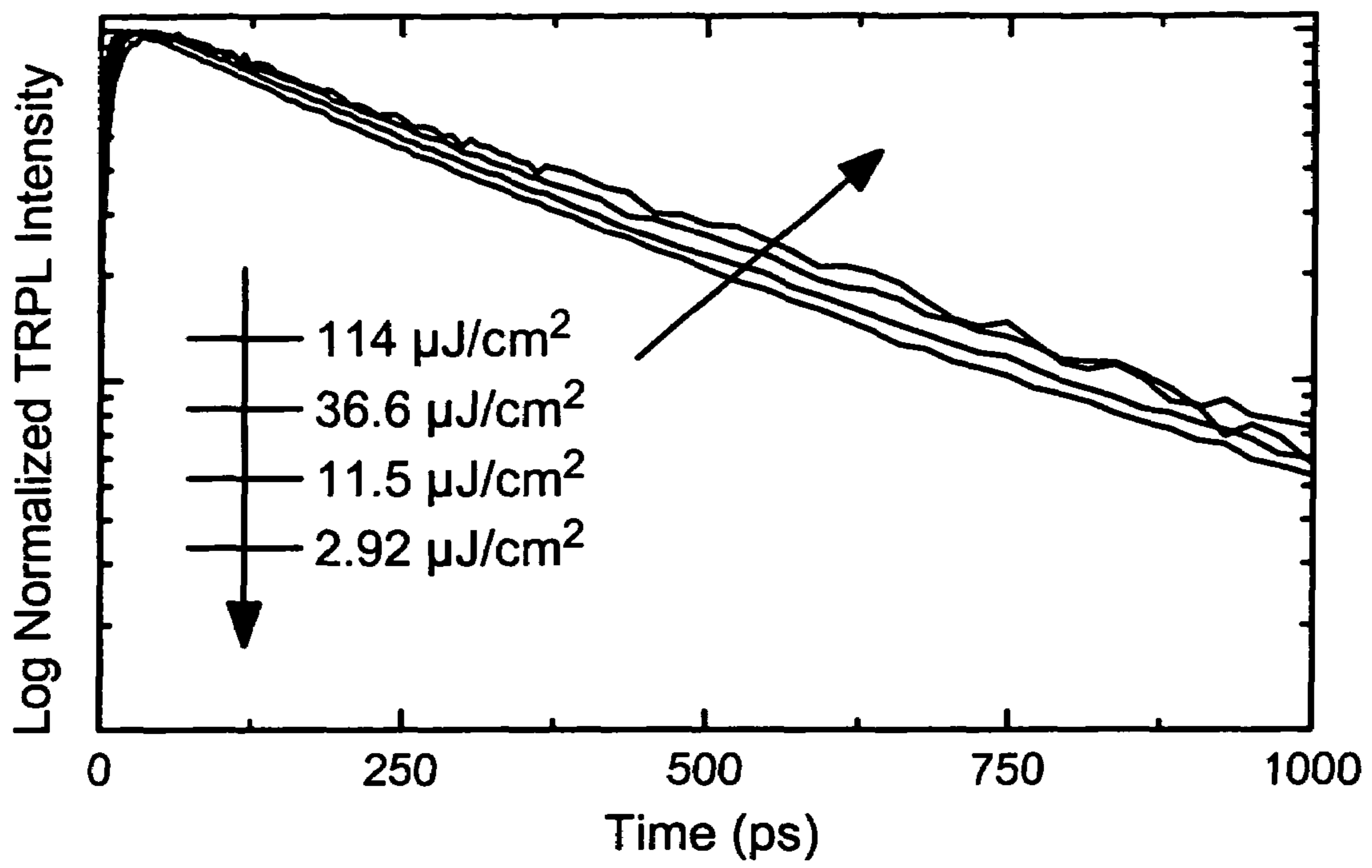


FIG. 26

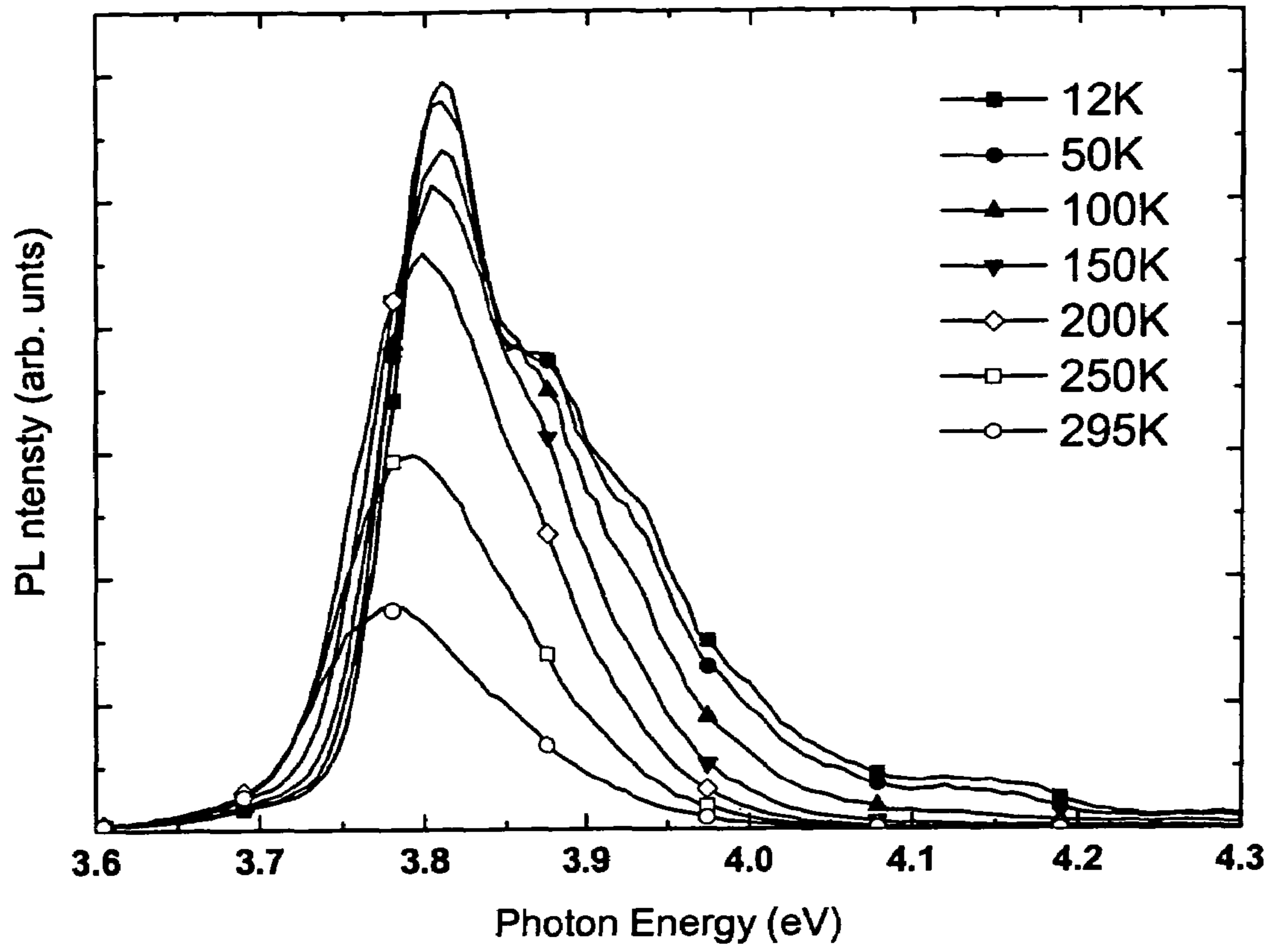


FIG. 27

**METHOD OF MANUFACTURING AN  
ULTRAVIOLET LIGHT EMITTING ALGAN  
COMPOSITION AND ULTRAVIOLET LIGHT  
EMITTING DEVICE CONTAINING SAME**

This application claims the priority of the corresponding provisional application Ser. No. 60/663,144, filed Mar. 18, 2005, the entire contents of which are incorporated herein by reference. This application is also related to application Ser. No. 11/376,453 filed on Mar. 15, 2006 for an Ultraviolet Light Emitting AlGa<sub>x</sub>N Composition, And Ultraviolet Light Emitting Device Containing Same.

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

The present invention provides an ultraviolet (UV) light emitting AlGa<sub>x</sub>N composition, a UV light emitting device, and a method of making both. In particular, a UV light emitting device is provided comprised of an active region layer composed of AlGa<sub>x</sub>N having localized nanoscale compositional inhomogeneities therein, as well as a manufacturing method for producing such an UV light emitting device.

BACKGROUND OF THE INVENTION

Conventionally, blue/violet LED's have been made using InGa<sub>x</sub>N alloys to produce the layers thereof. Problems encountered when fabricating optical sources using high dislocation density III-Nitride materials, such as InGa<sub>x</sub>N alloys, was first addressed during the development of LED's using the In<sub>x</sub>Ga<sub>1-x</sub>N alloy system. It was found that the material properties of InGa<sub>x</sub>N alloys change as the amount of indium in the alloy is increased. With the proper growth conditions, however, it was discovered that material could be grown in which the indium did not incorporate uniformly throughout the InGa<sub>x</sub>N layer (i.e., the material has areas of high and low concentrations of indium spread throughout). These compositional fluctuations, also known as localized inhomogeneities, result in carrier localization and lead to an enhancement in the radiative efficiency despite the high dislocation density.

The discovery of the effects of the localized inhomogeneities enabled the development of commercially successful blue InGa<sub>x</sub>N-based LEDs and laser diodes (LDs). See P. Waltereit, H. Sato, C. Poblenz, D. S. Green, J. S. Brown, M. Mclaurin, T. Katona, S. P. DenBaars, J. S. Speck, J. H. Liang, M. Kato, H. Tamura, S. Omori, and C. Funaoka, *Appl. Phys. Lett.* 84, 2748 (2004); S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, *Appl. Phys. Lett.* 67, 1868 (1995); S. Nakamura, *J. Vac. Sci. Technol. A* 13, 705 (1995); S. Nakamura, T. Mukai, M. Senoh, *J. Appl. Phys.* 76, 8189, (1994), each of which are incorporated herein by reference in their entireties.

Specifically, it has been reported that the intense red-shifted photoluminescence (PL) peaks observed in InGa<sub>x</sub>N alloys at room temperature result from the recombination of excitons localized at potential minima originating from large compositional fluctuations. See S. Chichibu, T. Azuhata, T. Sota, and S. Nakamura, *Appl. Phys. Lett.* 70, 2822 (1997); S. Chichibu, K. Wada, and S. Nakamura, *Appl. Phys. Lett.* 71, 2346 (1997); Y. Sun, Y. Cho, E. K. Suh, H. J. Lee, R. J. Choi, and Y. B. Hahn, *Appl. Phys. Lett.* 84, 49 (2004), each of which

are incorporated herein by reference in their entireties. Unfortunately, InGa<sub>x</sub>N alloys are not suitable for use in UV LED's at wavelengths shorter than 365 nanometers (nm).

A similar localization effect resulting from the creation of localized inhomogeneities has been reported for quaternary InAlGa<sub>x</sub>N alloys having an InN mole fraction of up to 20% and an AlN mole fraction of up to 60%, corresponding to light emission at wavelengths shorter than 365 nm. See E. Monroy, N. Gogneau, F. Enjalbert, F. Fossard, D. Jalabert, E. Bellet-Amalric, Le Si Dang, and B. Daudin, *J. Appl. Phys.* 94, 3121 (2003); Mee-Yi Ryu, C. Q. Chen, E. Kuokstis, J. W. Yang, G. Simin, and M. Asif Khan, *Appl. Phys. Lett.* 80, 3730 (2002); H. Hirayama, A. Kinoshita, T. Yamabi, Y. Enomoto, A. Hirata, T. Araki, Y. Nanishi, and Y. Aoyagi, *Appl. Phys. Lett.* 80, 207 (2002); C. H. Chen, Y. F. Chen, Z. H. Lan, L. C. Chen, K. H. Chen, H. X. Jiang, and J. Y. Lin, *Appl. Phys. Lett.* 84, 1480 (2004), each of which are incorporated herein by reference in their entireties. The carrier localization observed in such InAlGa<sub>x</sub>N quaternary materials is also attributed to indium segregation therein, resulting in enhanced luminescence at a peak wavelength significantly red-shifted (150-300 meV) with respect to the band edge.

The use of aluminum gallium nitride (Al<sub>x</sub>Ga<sub>1-x</sub>N), as opposed to InAlGa<sub>x</sub>N, is preferred as the base material for manufacturing UV LED devices due to the difficulty in growing device quality quaternary material (InAlGa<sub>x</sub>N). AlGa<sub>x</sub>N has, therefore, become the most important material for use in the development of ultraviolet semiconductor optical sources operating at wavelengths between 260 to 360 nm due to its tunable bandgap from 3.4 eV to 6.2 eV. Such sources have many useful military and commercial applications, including water purification, phosphor based white light sources, high-density data storage, bioagent detection and non-line of sight (NLOS) covert communication. See G. A. Shaw, A. M. Siegel, J. Model, and N. Nischan, *SPIE Defense & Security Symposium*, Vol. 5417, (2004), and E. Radkov, R. Bompiedi, A. M. Srivastava, A. A. Setlur, and C. A. Becket, *Proc. SPIE Int. Soc. Opt. Eng.*, Vol. 5187, 176, (2004), both of which are incorporated herein by reference in their entireties.

A major problem in manufacturing practical III-Nitride based sources, such as AlGa<sub>x</sub>N alloys, is the lack of a native substrate for the homoepitaxial growth of epilayers. Consequently, most devices are deposited heteroepitaxially on lattice mismatched substrates, like sapphire or SiC, with the resulting layer quality limited by the high density of threading dislocations produced therein. Such threading dislocations present in AlGa<sub>x</sub>N alloys deposited heteroepitaxially on lattice mismatched substrates are associated with non-radiative recombination centers that compete with radiative recombination paths, thus reducing the radiative recombination efficiency of these materials. One method for reducing the number of dislocations in III-nitride materials deposited by molecular beam epitaxy is to employ III-Nitride templates as a substrate that consists of an (In)(Ga)(Al)N thin film deposited upon a substrate, commonly sapphire or SiC, by a high temperature growth process (>1000° C.) such as metalorganic chemical vapor deposition or hydride vapor phase epitaxy.

With regard to optical sources, these threading dislocations present in AlGa<sub>x</sub>N alloys deposited heteroepitaxially on lattice mismatched substrates greatly reduce the wall plug efficiency (i.e., the ratio of the power of the light emitted versus the electrical power applied). Currently, the best reported UV light emitting diodes (LED) have very low wall plug efficiencies, ~1% or below, with the remaining input power being converted to heat. See A. Khan, *Light-Emitting Diodes: Research, Manufacturing, and Applications VII*, SPIE Vol.

4996, (2003); T. M. Katona, T. Margalith, C. Moe, M. C. Schmidt, S. Nakamura, J. S. Speck, S. P. DenBaars, *Third International Conference on Solid State Lighting*, SPIE Vol. 5187, (2004); K. B. Nam, J. Li, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* 84, 5264 (2004); S. Wiczorek, W. W. Chow, S. R. Lee, A. J. Fisher, A. A. Allerman, and M. H. Crawford, *Appl. Phys. Lett.* 84, 4899 (2004); M. H. Crawford, A. A. Allerman, A. J. Fisher, K. H. A. Bogart, S. R. Lee, R. J. Kaplar, W. W. Chow, and D. M. Follstaedt, *Light-Emitting Diodes: Research, Manufacturing, and Applications VIII*, SPIE Vol. 5366, (2004); A. Chitnis, J. Sun, V. Mandavilli, R. Pachipulusu, S. Wu, M. Gaevski, V. Adivarahan, J. P. Zhang, M. Asif Khan, A. Sarua, and M. Kuball, *Appl. Phys. Lett.* 81, 3491 (2002); V. Adivarahan, S. Wu, J. P. Zhang, A. Chitnis, M. Shatalov, V. Mandavilli, R. Gaska, and M. Asif Khan, *Appl. Phys. Lett.* 84, 4762 (2004); V. Adivarahan, W. H. Sun, A. Chitnis, M. Shatalov, S. Wu, H. P. Maruska, and M. Asif Khan, *Appl. Phys. Lett.* 85, 2175 (2004), each of which are incorporated herein by reference in their entireties.

The low wall plug efficiency further results in excessive heating of the UV LED material, which reduces the lifetime thereof, and may change the spectral and power output properties of UV LEDs. For these reasons, such UV LED devices are commonly pulsed in operation, such that the duty cycle is kept low enough to reduce undesirable heating effects on the UV LED material. Extracting the heat from these devices can also be challenging since the most commonly used substrate, sapphire, is a poor thermal conductor at room temperature. This difficulty in heat extraction requires elaborate packaging of the UV LED material, such as including flip-chip bonding of the final device to a thermally conductive substrate to help conductively dissipate the heat. These devices then emit light through the sapphire substrate, and are referred to as "back-emitters".

The red-shifts in the enhanced luminescence seen in In(Al) GaN quaternary alloys are much larger than those typically reported for  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys of comparable Al content (~10-50 meV). These  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys are referred to herein as band edge AlGaN alloys. Accordingly, it has been found that the large compositional fluctuations, i.e., localized inhomogeneities resulting in the desirable carrier localization that leads to an enhancement in the radiative efficiency, obtained using the current growth methods of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys do not occur when using such methods to grow  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys needed for the production of UV LEDs. In fact, it has been previously believed that AlGaN material systems cannot have unstable mixing regions (i.e., localized inhomogeneities) that would result in phase separation, as is the case for InGaN materials. See T. Matsuoka, Calculation of unstable mixing region in wurtzite InGaAlN, *Applied Physics Letters* 71, 105 (1997).

These smaller red-shifts found in the band edge  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys of comparable Al content (~10 to 50 meV) are often attributed to emission from bandtails associated with small alloy fluctuations and structural disorder. See Y. H. Cho, G. H. Gainer, J. B. Lam, W. Yang, W. Jhe, and J. J. Song, *Phys. Rev. B* 61, 7203 (2000); A. Bell, S. Srinivasan, C. Plumlee, H. Omiya, F. A. Ponce, J. Christen, S. Tanaka, A. Fujioka, and Y. Nakagawa, *J. Appl. Phys.* 95, 4670 (2004); H. S. Kim, R. A. Mair, J. Li, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.* 76, 1252 (2000), each of which are incorporated herein by reference in their entireties. While  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  on sapphire possesses long-lived low temperature photoluminescence (PL) on the order of 250-600 picoseconds (ps), a significant reduction in PL lifetime, to less than 20 ps at room temperature, is

generally observed due to thermally activated trapping and non-radiative recombination at defect sites in the  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloy.

These short room temperature lifetimes found in UV LED's comprising band edge  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  on sapphire correspond to low wall plug efficiencies, as discussed above. Without the availability of lattice matched substrates with reduced defect density, or the advantages of compositional fluctuations (i.e., localized inhomogeneities) found in InGaN alloys made using the conventional methods of production, production of efficient UV LED using band edge AlGaN alloys has been found to be practically impossible.

Most conventional UV LEDs are based on the same basic device structure. The substrate preparation and the nucleation steps for epilayer growth, however, are dependent upon the chemistry of the substrate used. These processes, as well as the subsequent buffer layers deposited, greatly affect the number of defects in the material. For example, in a conventional UV LED device structure, a thick silicon-doped n-type  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layer is grown to function as the bottom current-spreading layer of the UV LED device. For a back-emitter device, as described above, the AlN mole fraction of this current-spreading layer is made large enough to ensure that the current-spreading layer is transparent to the light emitted from the active region layer.

Next, a multiple quantum well (MQW) active region layer is deposited upon the current-spreading layer, with the number and thickness of the multiple quantum wells formed within the MQW layer depending on the particular device. This MQW layer is then generally capped with an AlGaN electron blocking layer, the AlGaN electron blocking layer optionally being doped p-type. Next, a p-type GaN contact layer is formed upon the AlGaN electron blocking layer. The p-type GaN contact layer is required due to the difficulties in doping AlGaN p-type.

The p-type GaN contact layer may optionally be replaced by many different AlGaN p-type layers depending on the particular device. If the MQW active region layer is replaced, for example, by an AlGaN layer with one aluminum percentage, then the device is called a double-heterostructure (DH) LED. While this conventional UV LED device structure is simple to grow, it is not possible to produce efficient DH-UV LEDs using the above-described method, due to the susceptibility of the active region layer to the non-radiative recombination centers typically found in these materials, polarization fields that tend to separate the electron hole pairs, and the lack of quantum confinement to improve electron-hole wave function overlap. The latter two reasons lead to a longer radiative lifetime in the bulk active layers that does not compete favorably with the nonradiative processes.

One method for depositing III-Nitride films is a technique called molecular beam epitaxy (MBE). This technique is a thin film deposition process in which thermal beams of atoms or molecules react on the clean surface of a substrate, held at high temperatures and under ultra-high vacuum conditions. The material sources for III-Nitride semiconductors traditionally consist of solid elemental constituent sources of gallium (Ga), aluminum (Al) and indium (In), that evaporate from the melt, as well as n- and p-type dopant sources silicon (Si) and magnesium (Mg) that sublime. Since molecular nitrogen ( $\text{N}_2$ ) does not crack on the substrate surface, plasma sources are employed to generate active nitrogen species from this gas source. Accordingly, this molecular beam epitaxy technique is commonly referred to as plasma-assisted molecular beam epitaxy (PA-MBE).

In this method, crystal growth is performed in a chamber with ultra-high vacuum ( $<10^{-9}$  Torr) base pressure (not

including the partial pressure of source gases) that allows for the deposition of high-purity materials at lower substrate temperatures than typically employed by vapor deposition techniques. This environment allows for the use of a number of in-situ probes, one of the most common being reflection high energy electron diffraction (RHEED). In this technique, a high energy (10 to 30 keV) electron beam is directed at the substrate at a grazing angle ( $\phi \approx 1^\circ$ ) with respect to the surface.

Since the penetration depth of the beam is only a few atomic layers, the crystalline surface acts as a two-dimensional grating that diffracts electrons. The diffraction pattern can be observed on a fluorescent screen located inside the MBE chamber. A film having a smooth surface, as illustrated in the SEM photograph representation of the conventional GaN layer grown at a high Ga flux shown in FIG. 1(a), is expected to have a pattern consisting of a series of streaks perpendicular to the substrate surface, as illustrated in FIG. 1(b), while a rough or polycrystalline film, as illustrated in the SEM photograph representation of a GaN layer grown at a low Ga flux, as illustrated in FIG. 2(a), would have a spotty pattern, as illustrated in FIG. 2(b).

Extensive work has been performed in this field on the growth of GaN using PA-MBE. It is known that two of the most important growth parameters for the deposition of high quality GaN epilayers are the substrate temperature and the group-III/group-V atomic flux ratio. Unlike the deposition of other III-V compounds by MBE, it is well known that high quality, smooth GaN films are deposited under a Ga-rich (N-limited) growth regime. This is due to the highly reactive nature of the active nitrogen species generated by the plasma source that results in very short adatom diffusion lengths.

Suitable parameter space for depositing GaN has been reported upon, and three distinct growth regimes identified, referred to as the N-stable, intermediate Ga stable and Ga droplets, as illustrated in FIG. 3 (See B. Heying, R. Averbek, L. F. Chen, E. Haus, H. Reichert, J. S. Speck, "Control of surface morphologies using plasma-assisted molecular beam epitaxy", *Journal of Applied Physics*, 88, 1855 (2000)). The boundary between the N-stable and the intermediate Ga stable regimes constitutes conditions that are nearly stoichiometric where the active nitrogen atom flux equals the Ga atom flux, and was determined by examining the dependence of the growth rate of the GaN film on the Ga atom flux.

The growth rate of GaN has been found to be independent of Ga atom flux (or Ga atom arrival rate) only within the intermediate Ga stable and Ga-rich regimes. Heavily Ga-rich growth conditions results in the accumulation of liquid Ga metal droplets on the surface of the film. Increasing the substrate temperature during growth has been observed to widen the range of Ga atom fluxes that result in intermediate Ga stable for a given active nitrogen flux.

As illustrated in FIG. 3, and as mentioned above, GaN film can be grown under three distinct growth regimes, i.e., the N-stable, intermediate Ga stable and Ga droplets. The surface morphology and optical properties of the GaN film have all been observed to depend upon the regime (method) of growth employed. Heying et al. have reported on the surface morphologies of GaN films deposited within each regime, and have observed that films deposited under N-stable conditions had morphologies that were rough and heavily pitted, while films grown within the intermediate regime had large flat areas between large irregularly shaped pits. In contrast, films deposited in the Ga droplet regime had atomically flat surfaces.

The present inventors have investigated the impact of III/V flux ratio on the continuous wave photoluminescence observed from GaN films, and have found that films grown

near stoichiometric conditions (i.e., where III/V flux ratio  $\sim 1$ ) had significantly more intense band-edge luminescence than films grown at higher III/V flux ratio. Similarly, the present inventors observed that films deposited near stoichiometric conditions had significantly longer photogenerated carrier lifetimes. These results are believed to be attributable to a high density of deep trap states in films deposited with higher III/V flux ratio.

In contrast to GaN, comparatively less has been reported on the growth of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  films by PA-MBE, which are useful in producing UV LED's. The present inventors have discovered that the AlN mole fraction of this ternary alloy ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ) is dependent upon the ratio of the Al/Ga atomic flux, the ratio of the total group III/group V atomic flux, as well as the substrate temperature. It has been previously observed that the AlN mole fraction of AlGaN alloys, deposited under constant Al/Ga atomic flux ratio, increases with increasing III/V flux ratio. This has been attributed to the preference for Al to incorporate into the film over Ga, due to the greater thermal stability of AlN over GaN. Presently, however, a growth diagram (methodology for production) for AlGaN alloys, comparable to the one developed for GaN as discussed above, has not been reported.

In view of the above, it is an object of the present invention to provide an AlGaN composition for use as an active region layer of a UV light emitting device, in which the active region layer's composition has localized inhomogeneities therein, resulting in carrier localization and enhanced radiative efficiency, and a UV light emitting device containing same.

It is a further object of the present invention to provide a method of manufacturing an AlGaN composition for use as an active region layer of a UV light emitting device, in which the active region layer has localized inhomogeneities formed therein, resulting in carrier localization and enhanced radiative efficiency, and a UV light emitting device containing same, as described above.

#### SUMMARY OF THE INVENTION

In order to achieve the objects of the present invention, as discussed above, the present inventors earnestly endeavored to overcome the difficulties in manufacturing a UV LED composition comprising AlGaN as the active region layer, and a method of producing such a composition and a device containing same. Accordingly, the present inventors have developed a method for manufacturing UV LED AlGaN composition active region layer having localized inhomogeneities resulting in carrier localization and enhanced radiative efficiency. As such, in a first embodiment of the invention, a method of manufacturing an ultraviolet light emitting device having a group III-Nitride active region layer containing an AlGaN alloy is provided, said method comprising:

depositing a layer of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  on a substrate or a film layer formed adjacent a substrate using plasma-assisted molecular beam epitaxy,

wherein the deposition of the layer of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is carried out under the following conditions:

- (a) deposition is performed under a faceted or three-dimensional growth regime;
- (b) the substrate temperature is maintained within a temperature range of from about 770 to 950° C.;
- (c) a nitrogen gas flow rate of from about 0.2 to 1.2 standard cubic centimeters per minute is maintained;
- (d) the layer of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is grown at a rate of about 80-1000 nm/hour;



- (e) the Al atom flux as measured by beam equivalent pressure is maintained at from about  $1 \times 10^{-8}$  to  $2 \times 10^{-7}$  Torr; and
- (f) the Ga atom flux as measured by beam equivalent pressure is maintained at from about  $2 \times 10^{-7}$  to  $2 \times 10^{-6}$  Torr, thereby producing an ultraviolet light emitting device having a group III-Nitride active region layer containing an AlGa<sub>x</sub>N alloy having nanometer-scale localized compositionally inhomogeneous regions therein.

In a second embodiment of the invention, the method of manufacturing of the first embodiment above is provided, wherein the layer of Al<sub>x</sub>Ga<sub>1-x</sub>N is deposited at a rate of from about 80 to 120 nm/hour.

In a third embodiment of the invention, the method of manufacturing of the first embodiment above is provided, wherein the nitrogen gas flow rate during the deposition of the layer of Al<sub>x</sub>Ga<sub>1-x</sub>N is maintained at from about 0.2 to 0.6 standard cubic centimeters per minute.

In a fourth embodiment of the invention, the method of manufacturing of the first embodiment above is provided, wherein the Al<sub>x</sub>Ga<sub>1-x</sub>N layer is doped with a dopant selected from the group consisting of silicon (Si), magnesium (Mg), beryllium (Be), germanium (Ge) or carbon (C).

In a fifth embodiment of the invention, the method of manufacturing of the fourth embodiment above is provided, wherein the Al<sub>x</sub>Ga<sub>1-x</sub>N layer is doped with an impurity in a concentration of from about  $10^{14}$  to  $10^{20}$  atoms/cm<sup>3</sup>.

In a sixth embodiment of the invention, the method of manufacturing of the fifth embodiment above is provided, wherein the Al<sub>x</sub>Ga<sub>1-x</sub>N layer contains an AlN mole fraction of about 33% and is doped with Si.

In a seventh embodiment of the invention, the method of manufacturing of the first embodiment above is provided, wherein:

- the Al<sub>x</sub>Ga<sub>1-x</sub>N is deposited atop an AlN buffer layer; and a Ga atom flux as measured by beam equivalent pressure of from about  $2 \times 10^{-7}$  to  $7 \times 10^{-7}$  Torr is employed.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1(a) is a digital representation of the surface morphology of a GaN layer grown at a high Ga flux.

FIG. 1(b) is a digital representation of a reflection high energy electron diffraction (RHEED) pattern observed for a GaN layer, the surface morphology is shown in FIG. 1(a).

FIG. 2(a) is a digital representation of the surface morphology of a GaN layer grown at a low Ga flux, according to the invention, produced by a scanning electron microscope (SEM).

FIG. 2(b) is a RHEED pattern observed for the GaN layer whose surface morphology is shown in FIG. 2(a).

FIG. 3 is graph of Ga-flux vs. substrate temperature, illustrating the three distinct growth regimes, referred to as the N-stable, intermediate Ga stable and Ga droplets. B. Heying, R. Averbek, L. F. Chen, E. Haus, H. Reichert, J. S. Speck, "Control of surface morphologies using plasma-assisted molecular beam epitaxy", Journal of Applied Physics, 88, 1855 (2000).

FIG. 4(a) is a digital representation of the surface morphology (obtained by a SEM) of an AlGa<sub>x</sub>N film produced at a low Ga atom flux of about  $3.3 \times 10^{-7}$ , as measured by beam equivalent pressure, according to the present invention, illustrating the fine scale, faceted surface morphology obtained with the method of the present invention, having surface pits on the order of about 10 to 100 nm wide.

FIG. 4(b) is a digital representation of the surface morphology (obtained by a SEM) of an AlGa<sub>x</sub>N film produced at a very

high Ga atom flux of about  $6.16 \times 10^{-7}$ , as measured by beam equivalent pressure, showing large scale faceting evidencing metal droplets.

FIG. 4(c) is a digital representation of the surface morphology (obtained by a SEM) of an AlGa<sub>x</sub>N film produced at a high Ga atom flux of about  $5.62 \times 10^{-7}$ , as measured by beam equivalent pressure, illustrating the smooth surface morphology of films produced at a high Ga atom flux.

FIG. 5 is a room-temperature monochromatic cathodoluminescence (CL) image of the group III-nitride containing AlGa<sub>x</sub>N alloy composition of the present invention, illustrating the luminescence obtained from the localized inhomogeneous regions of AlGa<sub>x</sub>N (i.e., areas of the AlGa<sub>x</sub>N composition in which the Al percentage varies) that are of smaller band gap energy than the surrounding material and act as radiative recombination centers.

FIG. 6 is cross sectional view of the semiconductor-based ultraviolet light emitting device of the present invention.

FIG. 7(a) is a perspective view of a semiconductor-based ultraviolet light emitting device of the present invention, wherein the device is structured as a laser diode (LD).

FIG. 7(b) is a perspective view of the single AlGa<sub>x</sub>N active region layer shown in FIG. 7(a).

FIG. 8(a) is a perspective view of a semiconductor-based ultraviolet light emitting device of the present invention, wherein the device is structured as a top and back emitting light emitting diode (LED).

FIG. 8(b) is a perspective view of the AlGa<sub>x</sub>N-containing active region layer shown in FIG. 8(a), wherein the active region layer consists of multiple AlGa<sub>x</sub>N layers of alternating band-edge AlGa<sub>x</sub>N and the AlGa<sub>x</sub>N alloy of the present invention having localized inhomogeneities present therein and having an AlN mole fraction smaller than the band edge AlGa<sub>x</sub>N alloy. Such a device is referred to as a multiple quantum well (MQW) LED structure.

FIG. 9 is a cross sectional view of a UV light emitting device of the present invention structured to operate as an LD (laser diode) using either optical carrier injection or electron beam carrier injection.

FIG. 10 is a cross sectional view of a carrier injection LED which is top emitting and bottom emitting, designed for injection of electrons or holes through a carrier injection pump.

FIG. 11 is a perspective view of an LD structure according to the present invention.

FIG. 12 is a cross sectional view of an LED structure according to the present invention.

FIG. 13 shows graphical illustrations of reflectivity, photoluminescence and corresponding digital representations of the surface morphology (obtained by SEM) for each of three Al<sub>x</sub>Ga<sub>1-x</sub>N alloys, all containing ~33% AlN by mole fraction. A digital representation of the surface morphology of each respective film is shown to the right of the reflectance and photoluminescence data thereof in the graph.

FIG. 14 is a graph illustrating the observed room temperature photoluminescence spectra for four AlGa<sub>x</sub>N films of the present invention, deposited at varying levels of Ga atom flux.

FIG. 15 is a graph of luminescence emission wavelength and alloy band gap energy for NCI AlGa<sub>x</sub>N alloys of the present invention having AlN mole fractions of from 27 to 60% as a function of Al atom flux (as measured by beam equivalent pressure).

FIG. 16 is a graph of relative integrated PL intensity vs. Si cell temperature for an AlGa<sub>x</sub>N alloy of the present invention containing 33% AlN by mole fraction.

FIG. 17(a) is a graphical illustration of the measured electroluminescence spectra (intensity vs. emission wavelength) of two DH-LEDs of the present invention utilizing an AlGaN template.

FIG. 17(b) is graphical illustration of the photoluminescence spectra (intensity vs. emission wavelength) of the NCI AlGaN active region layer that was incorporated into the DH-UV LEDs whose electroluminescence is presented in FIG. 17 (a).

FIG. 18 is a graphical illustration of the measured light output as function of DC drive current for an NCI—AlGaN DH-UV LED of the present invention, operating at 326 nm.

FIG. 19 is a graphical illustration of the measured electroluminescence spectra (intensity vs. emission wavelength) of a DH-LED of the invention utilizing a sapphire substrate.

FIG. 20 is a graphical illustration of the light output as function of DC drive current for an NCI—AlGaN DH-UV LED of the present invention, operating at 325 nm.

FIG. 21 is a graph comparing NCI—AlGaN active region layers deposited on nitride template and sapphire substrates versus conventional MQW active region layers deposited on nitride template and sapphire using time resolve photoluminescence studies (TRPL).

FIG. 22 is a graph comparing room-temperature PL data to reflectivity results for three different representative layers of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  thin films (i.e.,  $\text{Al}_{0.45}\text{Ga}_{0.55}\text{N}$ ,  $\text{Al}_{0.33}\text{Ga}_{0.67}\text{N}$ , and  $\text{Al}_{0.29}\text{Ga}_{0.71}\text{N}$ ) prepared according to the present invention, deposited directly on sapphire substrates.

FIG. 23 is a graph illustrating the PL spectra of the  $\text{Al}_{0.33}\text{Ga}_{0.67}\text{N}$  thin film sample shown in FIG. 22, at varying temperatures.

FIG. 24 is a graph illustrating the normalized TRPL measurements taken of the band edge photoluminescence (BE) in the  $\text{Al}_{0.33}\text{Ga}_{0.67}\text{N}$  thin film sample shown in FIG. 22 at room temperature after excitation of said film with a 290-nm laser pump pulse at four different fluences.

FIG. 25 is a graph illustrating the normalized TRPL measurements of the rise time of emission of the red-shifted photoluminescence (RS) in the  $\text{Al}_{0.33}\text{Ga}_{0.67}\text{N}$  thin film sample produced according to the present invention at room temperature, after excitation of said film with a 290-nm laser pump pulse at four different fluences.

FIG. 26 is a graph illustrating the log of the normalized TRPL measurements taken at the red-shifted photoluminescence (RS) peak of a  $\text{Al}_{0.33}\text{Ga}_{0.67}\text{N}$  thin film sample produced according to the present invention at room temperature, after excitation of said film with a 290-nm laser pump pulse at four different fluences.

FIG. 27 is a graph illustrating the variable temperature photoluminescence versus photon energy for a UV light emitting sample device of the present invention deposited on an hydride vapor phase epitaxy grown AlGaN template.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a semiconductor-based ultraviolet (UV) light emitting device active region AlGaN composition, for inclusion in a UV light emitting device operating at wavelengths of shorter than 360 nm. Further, the present invention provides a UV light emitting device comprised of a stack of layers that includes said active region layer, wherein light is generated through the radiative recombination of excited electron-hole pairs. These pairs can be created in the active region layer by either electrical injection, or by an optical/electron-beam pump. The active region layer is an aluminum gallium nitride ( $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ) based layer having localized inhomogeneities therein.

The present inventors further unexpectedly discovered a method of forming the active region layer's composition, so as to create these localized inhomogeneities, the inclusion of which results in improved wall plug efficiency for the device through enhancement of the radiative recombination efficiency in the active region layer, as well as enhanced light emission.

In particular, as illustrated in the scanning electron microscopy (SEM) image of the surface of an AlGaN film according to the present invention of FIG. 4(a) herein, the present invention provides UV light emitting device active region layer compositions comprised of aluminum and gallium containing III-Nitride alloys that exhibit enhanced photoluminescence (PL) lifetimes due to compositional fluctuations (i.e., localized inhomogeneities) therein. As shown in FIG. 4(a), the surface of an AlGaN film produced at a low Ga atom flux of about  $3.3 \times 10^{-7}$ , as measured by beam equivalent pressure, according to the present invention, has a fine scale, faceted surface morphology, having surface pits on the order of about 10 to 100 nm wide.

The compositional fluctuations, as illustrated in the room-temperature monochromatic cathodoluminescence (CL) image of the AlGaN active region layer of the present invention of FIG. 5 herein, are nanometer scale, compositionally inhomogeneous regions of AlGaN (i.e., areas of the AlGaN composition in which the Al percentage varies) that are of smaller band gap energy than the surrounding material and act as radiative recombination centers.

These aluminum and gallium containing III-Nitride alloys function as the active region layer in UV light emitting semiconductor layer stacks commonly referred to as ultraviolet light devices. Such devices, and methods for manufacturing same by depositing the active region layer alloys under a faceted and/or three-dimensional growth mode, are provided herein.

In contrast, conventionally, AlGaN films are produced at a very high Ga atom flux of, for example, about  $6.16 \times 10^{-7}$  (as measured by beam equivalent pressure), which may lead to a surface morphology having large scale faceting evidencing metal droplets, as illustrated in FIG. 4(b). Alternatively, as illustrated in FIG. 4(c), the surface of an AlGaN film produced at a high Ga atom flux of about  $5.62 \times 10^{-7}$  (as measured by beam equivalent pressure), may have a smooth surface morphology.

As illustrated in FIG. 6, the active region layer of the present invention as described above may be incorporated into a semiconductor UV light emitting diode (UVLED) 10 of the present invention comprising a substrate 12, an AlN buffer layer 14 deposited atop the substrate 12, and a silicon doped n-type  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  current spreading layer 16 grown atop the AlN buffer layer 14. The AlN buffer layer is optionally provided, and not used when employing a nitride substrate or template. An active region layer 18, comprised of the group III-Nitride containing AlGaN alloy having nanometer-scale localized compositionally inhomogeneous regions therein of the first embodiment herein, is epitaxially grown atop the current spreading layer 16. The active region layer 18 is capped with an AlGaN electron blocking layer 20 and a p-type GaN contact layer 22.

The substrate may be a sapphire substrate, a group III-V nitride substrate or template on a sapphire substrate, a SiC semiconductor substrate, a GaAs semiconductor substrate, an InP semiconductor substrate, a ZnO semiconductor substrate, an elemental Si semiconductor substrate, an elemental Ge semiconductor substrate or any other substrate upon which a single crystal III-Nitride film may be grown. The AlGaN electron blocking layer 20 may or may not be doped p-type.

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An n-electrode **24** and a p-electrode **26** are provided for connectivity.

The active region layer **18** may, as illustrated in FIGS. **7(a)** and **7(b)**, consist of a single group III-Nitride active region layer containing an AlGa<sub>N</sub> alloy having nanometer-scale localized compositionally inhomogeneous regions therein. If the active region layer of the semiconductor UV LED is grown as a single AlGa<sub>N</sub> layer with an aluminum percentage that is substantially the same as the band-edge n-AlGa<sub>N</sub> layer beneath it and the band-edge p-AlGa<sub>N</sub> layer above it, then the semiconductor device is referred to as a homojunction LED structure.

In a preferred embodiment of the present invention, as illustrated in FIGS. **7(a)** and **7(b)**, the active region layer **18** of the UV LED **10** is a single AlGa<sub>N</sub> layer grown with an aluminum percentage that is less than the n-AlGa<sub>N</sub> layer below and the p-AlGa<sub>N</sub> layer above. Such a device is referred to as a double-heterojunction (DH) LED structure.

In another preferred embodiment of the present invention, as called for in the fourteenth embodiment herein and as illustrated in FIGS. **8(a)** and **8(b)**, the active region layer **18** of the UV light emitting device **10** may consist of multiple layers of band-edge AlGa<sub>N</sub> with alternating AlN mole fractions. For example, one period of such a structure would consist of one layer of AlGa<sub>N</sub> with a higher Al percentage and a wider bandgap, and one layer with a lower Al percentage and a smaller bandgap. Both of these layers may contain the nanoscale compositional inhomogeneities described in the first embodiment herein or, alternatively, only the smaller bandgap material may contain them. Such a device is referred to as a multiple quantum well (MQW) or superlattice LED structure.

The UV light emitting device of the present invention may be structured to operate as an LD (laser diode), as shown in FIG. **9**, or as an LED, as shown in FIG. **10**, using either optical carrier injection or e-beam carrier injection. As shown in FIG. **9**, an LD **44** is designed for injection of electrons or holes through a carrier injection pump **50**. The carrier injection pump **50** may be an optical pump or an e-beam pump. A first band-edge AlGa<sub>N</sub> layer **46** which may comprise one or multiple layers, **46** is deposited on the substrate **12** and an optional AlN buffer layer **14** if required.

Optionally, (Al)(In)(Ga)N could be used in place of AlN for the buffer layer **14**. The active region layer **18** is formed on the band-edge AlGa<sub>N</sub> layer **46**, and a second band-edge AlGa<sub>N</sub> layer **48** is formed on the active region layer **18**. The band-edge AlGa<sub>N</sub> layers **46** and **48** have a higher Al content than that of the active region layer matrix to ensure waveguiding of the emitted light. The LD **44** is an edge-emitting device, as illustrated by the UV laser output **52**.

FIG. **10** illustrates an LED **54** which, like the LD **44** shown in FIG. **9**, is also designed for injection of electrons or holes through a carrier injection pump **50**. The LED structure is formed similarly to the LD structure, i.e., via depositing a first band-edge AlGa<sub>N</sub> layer **46** on a substrate **12** and an optional AlN buffer layer **14** if required. The active region layer **18** is formed on the band-edge AlGa<sub>N</sub> layer **46**, and a second band-edge AlGa<sub>N</sub> layer **48** is formed atop the active region layer **18**. In contrast to the LD device, however, the carrier injection LED **54** is capable of top-emitting, illustrated by light emission **56**, and/or bottom-emitting, illustrated by light emission **58**.

If the carrier injection pump **50** is an optical pump, such that the carrier injection LD **44** and the carrier injection LED **54** are optically injected, then the AlGa<sub>N</sub> active region layer **18** or the surrounding layers, band-edge AlGa<sub>N</sub> layer **46** and band-edge layer **48**, absorb the light from the optical pump,

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generating electron hole pairs. The generated electrons and holes can then recombine in the active region layer **18** to produce light.

The carrier injection pump **50** can also be an e-beam source. Using an electron beam source, the energetic electrons are injected into the active region layer **18** and/or the surrounding layers, band-edge AlGa<sub>N</sub> layer **46** and band-edge layer **48**, and collide with electrons in the atoms with enough energy to cause the electrons to break free from the atoms. This produces electron hole pairs, similar to the optical pumping above, that can then recombine in the active region layer **18** to produce light.

Two common electrically injected devices are laser diodes (LD), as shown in FIG. **9** and FIG. **11**, and light-emitting diodes (LEDs), as shown in FIG. **10** and FIG. **12**. As illustrated in FIG. **11**, the present invention provides an LD **28** structure **28** formed by sandwiching the active region layer **18** between an n-type semiconductor layer **32** and a p-type semiconductor layer **34**, thus creating a p-n junction photodiode. The n-type semiconductor layer **32** may contain superlattices to improve current spreading and injection, and may contain some layers of a wider bandgap for waveguiding the emission.

The p-type semiconductor layer **34** may contain a wider bandgap electron blocking layer and other wider bandgap layers for waveguiding. The p-type semiconductor layer **34** may also contain superlattices to improve current spreading and injection. The electrons and holes are injected through the ohmic contacts into the active region layer **18** via the semiconductor layers **32** and **34**, creating an electrically injected device.

The LD **28** shown in FIG. **11** is formed by optionally depositing an AlN buffer layer **14** on a suitable substrate **12**, such as sapphire. An n-type semiconductor layer **32** is then deposited upon the AlN buffer layer **14**. An AlGa<sub>N</sub> active region layer **18**, as described above, is then deposited on the n-type semiconductor layer **32**. A Mg doped p<sup>+</sup> semiconductor layer **34** is formed upon the active region layer **18**. An n-electrode **24** formed upon the n-type semiconductor layer **32**, and a p-electrode **26** formed upon the Mg doped p<sup>+</sup> semiconductor layer **34**, are deposited for connectivity of the LD **28** to an injection source. The LD **28**, shown in FIG. **11**, is an edge-emitting device, as illustrated by the UV laser emission **30** therefrom.

The LED **38**, shown in FIG. **12**, is similarly formed by optionally depositing an AlN buffer layer **14** on a suitable substrate **12**. An n-type semiconductor layer **32** is then deposited upon the AlN buffer layer **14**. An AlGa<sub>N</sub> active region layer **18**, as described above, is deposited upon the n-type semiconductor layer **32**. A Mg doped p<sup>-</sup> semiconductor layer **34** of wider bandgap is deposited upon the active region layer **18** as an electron blocking layer. A Mg doped p<sup>+</sup> semiconductor layer **36** is then formed on the Mg doped p<sup>-</sup> semiconductor layer **34**.

An n-electrode **24** and a p-electrode **26** are provided on the n-type semiconductor layer **32** and the Mg doped p<sup>+</sup> semiconductor layer **36**, respectively, for connectivity of the device to an injection source. In contrast to the LD **28** shown in FIG. **11**, the LED **38** shown in FIG. **12** may be top-emitting, as illustrated by the light emission **40**, and/or bottom-emitting, as illustrated by the light emission **42**.

As discussed above, the LD **28** and the LED **38** have similar layer structures, with varied thickness depending on whether it is an edge-emitting LD **28** or a top-emitting and/or bottom-

emitting LED **38** structure. Both LD **28** and LED **38** can be grown with multiple arrangements of the AlGa<sub>x</sub>N active region layer **18**.

For a single AlGa<sub>x</sub>N layer as disclosed earlier, when forming an active region layer of a semiconductor device as a single AlGa<sub>x</sub>N layer grown with an aluminum percentage that is substantially the same as the band-edge n-AlGa<sub>x</sub>N layer beneath it and the band-edge p-AlGa<sub>x</sub>N layer above it, the semiconductor device is referred to as a homojunction LED structure.

#### Methods of Production

Inventors unexpectedly discovered a regime (process) for growing ternary Al<sub>x</sub>Ga<sub>1-x</sub>N alloys by PA-MBE that results in films thereof having nanometer scale compositional inhomogeneities therein. These localized compositional inhomogeneities, as illustrated in FIG. **5** herein, provide the beneficial effect of promoting radiative recombination (generation of light) in regions of smaller AlN mole fraction (and lower energy) over non-radiative recombination in the larger AlN mole fraction matrix.

In particular, the invention provides methods for producing UV light emitting devices containing the Al<sub>x</sub>Ga<sub>1-x</sub>N alloy composition described above as the active region layer. Such methods of producing these devices, in general, may involve, when using a sapphire substrate, deposition of a plurality of films sequentially on the substrate using a process comprising nitridation, high temperature AlN buffer deposition, prior to the epilayer growth of the AlGa<sub>x</sub>N active region and band-edge layers. In particular, PA-MBE may be used.

The active region and band-edge layers may be deposited in various orders. Importantly, the method of the present invention allows creation of localized inhomogeneities in the AlGa<sub>x</sub>N active region layer that contain nanometer-scale areas having larger or smaller AlN mole fraction than the entire composition on average by the growth of the film under a faceted or three-dimensional growth mode. This growth mode is achieved while growing under conditions where the growth rate of the film is determined by the arrival rate of active nitrogen (N-limited).

Further, this growth mode is achieved by growing under nearly stoichiometric conditions where the ratio of the arrival rate of group-III atoms (Al, Ga) and the arrival rate of active nitrogen is about unity. Moreover, the nanometer scale compositional inhomogeneities are self-assembled within the film as a result of the growth mode. The present process/method that results in the growth mode for producing a film comprised of an Al<sub>x</sub>Ga<sub>1-x</sub>N alloy, utilizable as an active region layer of a UV light emitting device, is defined by the following process factors:

1. Substrate temperature
2. Group-III atom flux (Al and Ga)
3. N atom flux/Growth Rate
4. Doping concentration

#### Substrate Temperature

The present inventors have investigated a large range of substrate temperatures, and have discovered that the optimum substrate temperature range for formation of nanoscale compositional inhomogeneities in AlGa<sub>x</sub>N (NCI—AlGa<sub>x</sub>N) in films deposited by the method of the present invention is between 770 to 950° C., as measured by the substrate thermocouple. Preferably, a substrate temperature of about 880 to 900° C. is maintained.

#### N Atom Flux/Growth Rate

Films deposited by the process/method of the present invention are grown under N-limited conditions, wherein the growth rate of the AlGa<sub>x</sub>N film is dependent upon the arrival rate of active nitrogen on the substrate. The arrival rate of nitrogen in the present method is dependent upon the RF plasma power and the flow rate of N<sub>2</sub> gas employed.

The present inventors have deposited NCI—AlGa<sub>x</sub>N at a growth rate of as high as 220 nm/hr, which corresponds, in their reactor, to a RF plasma power of about 300W, and a N<sub>2</sub> gas flow rate of about 0.6 sccm (standard cubic centimeters per minute). This is equivalent to an effective nitrogen flux of 0.09 to 0.238 monolayers/sec. However, NCI—AlGa<sub>x</sub>N may be deposited at a growth rate of about 1000 nm/hr using an RF plasma source.

#### Group-III Atom Flux (Al and Ga)

The amount of total group-III flux for a given effective nitrogen flux is the most important growth parameter in promoting the formation of nanoscale compositional inhomogeneities in the Al<sub>x</sub>Ga<sub>1-x</sub>N alloys of the present invention. In the present invention, the total Al flux for a given effective nitrogen flux, to promote the formation of nanoscale compositional inhomogeneities in the Al<sub>x</sub>Ga<sub>1-x</sub>N alloys, is from  $1 \times 10^{-8}$  to  $2 \times 10^{-7}$  Torr, as measured by beam equivalent pressure. The total Ga flux, as measured by beam equivalent pressure, is from  $2 \times 10^{-7}$  to  $2 \times 10^{-6}$  Torr. In a preferred embodiment of the invention, the Al atom flux, as measured by beam equivalent pressure, is from  $1 \times 10^{-8}$  to  $4 \times 10^{-8}$  Torr, and the Ga atom flux, as measured by beam equivalent pressure, is from  $2 \times 10^{-7}$  to  $7 \times 10^{-7}$  Torr.

FIG. **13** graphically illustrates reflectivity, photoluminescence and scanning electron microscopy (SEM) data for three Al<sub>x</sub>Ga<sub>1-x</sub>N alloys of the present invention (the SEM photos of each film shown to the right of the reflectance and photoluminescence data therefor in the graph), all containing ~33% AlN by mole fraction. The Al and Ga atom flux for this process/method is given as beam equivalent pressure that is directly proportional to the atom flux and is directly measurable inside the reactor. All of the films were deposited at a constant substrate temperature of about 880° C. and with equivalent Al atom flux of about  $1.4 \times 10^{-8}$  Torr as measured by beam equivalent pressure, as well as an active nitrogen flux of about 0.09 monolayers/sec (250W RF power, 0.25 sccm flow rate).

As illustrated in FIG. **13**, the photoluminescence observed for the AlGa<sub>x</sub>N alloys deposited at the Ga atom fluxes greater than about  $5.6 \times 10^{-7}$  Torr, as measured by beam equivalent pressure, is dominated by near band edge emission, which is typical of what is generally observed for these alloys and which we refer to as “band-edge AlGa<sub>x</sub>N”. The surface morphology of these films is smooth, with the film deposited at the highest BEP (beam equivalent pressure), shown at the top of FIG. **13**, showing evidence of metal droplet formation.

In contrast, the photoluminescence peak of the AlGa<sub>x</sub>N alloy film deposited with the lowest Ga atom flux, as measured by beam equivalent pressure, of about  $3.34 \times 10^{-7}$  Torr is at a significantly lower energy than the band gap of the film (as great as 400 meV) and displays a luminescence significant intensity enhancement (~1000×) as shown in FIG. **14**. The surface of such AlGa<sub>x</sub>N alloy film, as illustrated at the bottom of FIG. **13**, is characterized by a faceted morphology consisting of small pits having diameters of smaller than about 60 nm. The present inventors have grown such NCI—AlGa<sub>x</sub>N alloys utilizing a Ga atom flux of between  $2.00 \times 10^{-7}$  and  $7 \times 10^{-7}$  Torr (as measured by beam equivalent pressure).

The AlN mole fraction of the NCI—AlGaN alloy and therefore the average AlN mole fraction of the film can be varied by changing the Al atom flux employed during growth. FIG. 15 illustrates the emission wavelength and corresponding band gap energy for such NCI AlGaN alloys of the present invention having AlN mole fractions of from 27 to 60% as a function of Al atom flux (as measured by Al BEP). The Ga atom flux must also be appropriately adjusted, so that approximately stoichiometric growth conditions are obtained, insuring an optimal result. An energy-shift greater than 250 meV and a corresponding enhanced luminescence efficiency has been observed throughout this compositional range.

NCI (nanoscale compositionally inhomogeneous) AlGaN alloys (i.e., a group III-Nitride containing AlGaN alloy having nanometer-scale localized compositionally inhomogeneous regions therein) having an AlN mole fraction of between about 20 to 80% can be obtained using the present method. Varying the composition of the matrix of the AlGaN alloy during the deposition process described above allows tuning of the wavelength of the luminescence emission of the device, as desired, as shown in FIG. 15. The inventors have demonstrated tunability within the wavelength region of from 255 to 340 nm. All of the AlGaN active region layer alloys grown using the present method exhibit enhanced luminescence efficiency through carrier localization, without the use of indium.

#### Doping Concentration

Inventors investigated the doping of NCI AlGaN with silicon (Si) to determine the effect thereof. As illustrated in FIG. 16, at Si concentrations of up to  $10^{19}$  atoms/cm<sup>3</sup>, relative integrated photoluminescence intensity is increased by doping of the AlGaN layer with silicon. In particular, it was unexpectedly discovered that greater enhancement of the photoluminescence can be obtained by doping with Si, with an impurity concentration of about  $2 \times 10^{17}$  atoms/cm<sup>3</sup> having been found preferable for an alloy containing 33% AlN by mole fraction.

The Al<sub>x</sub>Ga<sub>1-x</sub>N alloy thin films of the present invention are preferably deposited by plasma-assisted molecular beam epitaxy (PA-MBE) using, for example, a VARIAN™ GenII MBE reactor. This reactor has three zones commonly referred to as the entry chamber, the preparation chamber, and the growth chamber, all being maintained at ultra-high vacuum ( $<10^{-9}$  Torr) to provide a clean environment for semiconductor crystal growth. The entry chamber and preparation chamber are used for in-situ cleaning of the substrate upon which the AlGaN epilayer is to be grown. The Al<sub>x</sub>Ga<sub>1-x</sub>N thin films are deposited in the growth chamber, equipped with effusion cells, for the evaporation of the group-III constituents, gallium (Ga) and aluminum (Al), as well as the n-type dopant, silicon (Si). The arrival rate of these atoms at the substrate is controlled by regulating the temperature of the effusion source, and monitored by measuring the atom beam equivalent pressure (BEP). A radio frequency (RF) plasma source is employed to turn nitrogen gas (N<sub>2</sub>) into active nitrogen. The arrival rate of these nitrogen species on the substrate is controlled by adjusting the RF power of the plasma and the gas flow rate.

In the film deposition processes of the present method, flow rates and RF plasma powers are adjusted to achieve the conditions of the present method as set forth above. For example, a flow rate of about 0.25 sccm and a RF plasma power of about 250W may be employed. High purity elemental source materials for Ga, Al and Si (99.9999% or better), as well as high

purity N<sub>2</sub> gas (99.9995%), are preferably utilized in the process of the present invention, so as to reduce the incorporation of undesirable impurities.

The invention is shown by way of example.

#### EXAMPLE 1

A DH (double heterostructure) UV-LED was fabricated according to the present method, using PA-MBE as described above. In particular, a n-type AlGaN current spreading layer having an AlN mole fraction of about 40% and a thickness of approximately 50 nm was deposited upon an AlGaN template. This n-type AlGaN current spreading layer was deposited under nitrogen limited conditions at a growth rate of about 220 nm/hr using nitrogen plasma conditions of about 300W rf power and about 0.6 sccm N<sub>2</sub> gas flow rate. The substrate temperature employed was about 891° C., and the Al and Ga atom flux (as measured by BEP) were approximately  $5.14 \times 10^{-8}$  and  $2.07 \times 10^{-7}$  Torr respectively. The layer was intentionally doped n-type by incorporating about  $1 \times 10^{19}$  atoms/cm<sup>3</sup> of silicon into the film by employing a Si effusion cell temperature of 1220° C.

Subsequently, an active region layer was deposited on top of the n-type AlGaN current spreading layer under nearly stoichiometric and nitrogen limited conditions, so as to encourage the formation of a faceted surface morphology of the active region layer during growth, as called for by the present invention. The active region layer consists of an AlGaN alloy having nanometer scale compositional inhomogeneities and having an average AlN mole fraction of about 33%. In particular, a growth rate of about 80 nm/hr was employed using nitrogen plasma conditions of about 250W rf power and about 0.25 sccm N<sub>2</sub> gas flow rate. The substrate temperature employed was about 899.7° C. and the Al and Ga atom flux (as measured by BEP) were approximately  $1.87 \times 10^{-8}$  and  $4.24 \times 10^{-7}$  respectively. The layer was intentionally doped n-type by incorporating about  $2 \times 10^{17}$  atoms/cm<sup>3</sup> of silicon into the film by employing a Si effusion cell temperature of 1100° C. Thereafter, the heterostructure wafer was then cooled to 20° C. at a rate of about 3 C/min and subsequently removed from reactor. Next, the active region layer was examined by photoluminescence studies prior to the wafer being sent to a commercial partner for the deposition of a p-type AlGaN blocking layer having an AlN mole fraction about 40% and a p-GaN layer using proprietary processes to complete the DH-UVLED structure as described in the tenth embodiment of the present invention.

DH UV LEDs designed for electrical injection were fabricated utilizing this material by our commercial partner using proprietary processes. Devices having areas of 100×100 and 200×200 μm<sup>2</sup> were fabricated, and their measured electroluminescence spectra is shown in FIG. 17 (a). These devices were observed to have a peak emission wavelength of about 326 nm, which is consistent with the photoluminescence measurements performed prior to completion of the DH-UVLED structure (FIG. 17(b)), and is evidence that the electroluminescence originates from the NCI active region layer of the present invention.

Standard electroluminescence intensity vs DC drive current measurements were performed on these devices and their results are shown in FIG. 18. It was observed that the smaller device (having an area of 100×100 μm<sup>2</sup>) had an optical power output of 0.45 mW at 80 mA DC drive current. It should be

noted that the data was measured by examining an unpackaged chip, and thus the power output may be understated.

## EXAMPLE 2

A DH (double heterostructure) UV-LED was fabricated according to the present method, using PA-MBE and utilizing a sapphire substrate as described above. First, the substrate was nitridated by heating to a temperature 831.6° C., and then the surface of the substrate was exposed to the nitrogen plasma source for 10 minutes. The plasma source conditions for this step were 300W rf power and 0.6 sccm. Thereafter, an AlN buffer layer, with an approximate thickness of 25 nm, was deposited atop the nitridated substrate utilizing an Al atom flux (as measured by BEP) of about  $5.02 \times 10^{-8}$  Torr and a growth rate of 220 nm/hr. The substrate temperature and nitrogen plasma conditions for this step were identical to that of the nitridation step.

Subsequently a n-type AlGaIn current spreading layer having an AlN mole fraction of about 40% and thickness of about 1800 nm was deposited under nitrogen-limited conditions using a substrate temperature, growth rate and plasma source condition identical to the AlN buffer layer step. The Al and Ga atom flux (as measured by BEP) employed during this step were approximately  $1.87 \times 10^{-8}$  and  $4.24 \times 10^{-7}$  Torr, respectively. The layer was intentionally doped n-type by incorporating about  $1 \times 10^{19}$  atoms/cm<sup>3</sup> of silicon into the film by employing a Si effusion cell temperature of 1220° C.

Subsequently, an active region was deposited under nearly stoichiometric and nitrogen limited conditions so as to encourage a faceted surface morphology during growth, as called for by the present invention. The active region layer consisted of an AlGaIn alloy having nanometer scale compositional inhomogeneities, and having an average AlN mole fraction of about 33%. This active region layer was approximately 50 nm thick, and deposited at a growth rate of about 80 nm/hr.

The nitrogen plasma conditions employed consisted of a 250W rf power and about 0.25 sccm N<sub>2</sub> gas flow rate. The substrate temperature employed was about 876.1° C. and the Al and Ga atom flux (as measured by BEP) were approximately  $1.89 \times 10^{-8}$  and  $6.17 \times 10^{-7}$  Torr, respectively. The active region layer was intentionally doped n-type by incorporating about  $2 \times 10^{17}$  atoms/cm<sup>3</sup> of silicon into the film by employing a Si effusion cell temperature of 1100° C.

As a next step, an electron blocking layer, consisting of 10 nm of AlGaIn and having an AlN mole fraction of about 40%, was deposited under identical conditions to that of the n-type AlGaIn current spreading layer, with one notable exception. The electron blocking layer was doped with magnesium instead of silicon, using a Mg atom flux (as measured by BEP) of  $6.82 \times 10^{-8}$  Torr. Finally, a 220 nm thick p-type GaN layer was deposited under nitrogen limited conditions at a substrate temperature of 831.6° C., a Ga atom flux (as measured by BEP) of  $6.75 \times 10^{-7}$  Torr and a Mg atom flux (as measured by BEP) of  $6.82 \times 10^{-8}$  Torr. The growth rate and plasma source conditions employed were identical to those used for the deposition of the n-AlGaIn current spreading layer. The DH UVLED structure was then cooled to 20° C. at a rate of about 3° C./min.

The DH UV LEDs designed for electrical injection were fabricated by the inventors having an area of  $1 \times 1$  mm<sup>2</sup>. The measured electroluminescence from the fabricated devices was observed to peak at 325 nm as shown in FIG. 19. Standard electroluminescence intensity vs. DC drive current measurements were performed on these devices and their results are shown in FIG. 20. It was observed that these devices had an

optical power output of 25 μW at 60 mA DC drive current. It should be noted that the data was measured by examining an unpackaged chip, and thus the power output may be understated.

## EXAMPLE 3

FIG. 21 shows a comparison of the photoluminescence lifetime in NCI AlGaIn active region layers of present invention versus conventional AlGaIn MQW (multiple quantum well) active region layers, deposited on both sapphire and a nitride semiconductor template. The conventional AlGaIn MQW active region layers were designed for emission at 330 to 340 nm. They were deposited on a thin GaN template (buffer) on sapphire, and on a thick GaN HVPE free-standing substrate. The defect densities for the thin GaN template and the thick GaN substrate were estimated from etch pit counting by atomic force microscopy (AFM) to be  $\sim 10^9$  cm<sup>-2</sup> and  $10^7$  cm<sup>-2</sup>, respectively.

It was found that the PL lifetime in the AlGaIn MQW on the thin GaN template is about 100 ps, while for the AlGaIn MQW on the thick GaN substrate the PL lifetime increases to about 500 ps (see G. A. Garrett, C. J. Collins, A. V. Sampath, H. Shen, M. Wraback, S. F. LeBoeuf, J. Flynn, and G. Brandes, *Phys. Stat. Sol.(c)* Vol. 2, No. 7, pp. 2332-2336 (2005), incorporated by reference in its entirety herein). FIG. 21 clearly shows that the NCI AlGaIn active region layer of the present invention on sapphire has a much longer PL lifetime (about 400 ps) than its conventional AlGaIn MQW counterpart on the thin GaN template, despite having about two orders of magnitude higher defect density.

FIG. 21 further clearly shows that the NCI AlGaIn active region layer on an AlGaIn template, with a defect density greater than  $10^9$  cm<sup>-2</sup>, has a significantly longer PL lifetime (about 700 ps) than the conventional AlGaIn MQW active region layer deposited on a GaN template with more than two orders of magnitude lower defect density. Since PL lifetime is directly related to radiative efficiency in these cases, these results provide further proof of the vastly improved radiative efficiency of the NCI AlGaIn of the present invention over that of conventional AlGaIn MQWs, despite a higher density of defects associated with nonradiative channels in the NCI AlGaIn.

## EXAMPLE 4

## Preparation

The deposition of high quality III-Nitride materials by the PA-MBE process requires proper preparation of the substrate surface immediately prior to growth to remove contamination that would otherwise degrade the quality of the epitaxial layer. These preparation techniques consist of both in-situ (within the MBE reactor) and ex-situ (outside the MBE reactor) steps meant to condition the surface of the substrate. A 2 inch diameter, single side polished, substrate was prepared ex-situ by first evaporating an approximately 2 micron thick titanium film on the back-side of the substrate by sputter deposition. Subsequently, this titanium film was capped with an approximately 1 micron thick silicon dioxide film deposited by plasma enhanced chemical vapor deposition (PECVD). The 2 inch diameter substrate was then cut into 4 similar size pieces using a dicing saw equipped with a diamond blade.

These 4 smaller sized substrates were chemically prepared by solvent degreasing in acetone, methanol, and finally 2-propanol, for about 20 minutes each. Next, the substrates were

rinsed with deionized water (DI-H<sub>2</sub>O), and then immersed in a boiling 3:1 hydrochloric acid to nitric acid solution for about 10 minutes. The protective PECVD-deposited oxide cap previously formed on the titanium cap was then removed by immersing each substrate in 6:1 buffer oxide etchant. The substrates were then rinsed again in DI-H<sub>2</sub>O for 30 minutes prior to mounting on a substrate holder. The samples were mounted into standard 3 inch VARIAN™ molybdenum blocks using an Applied EPI™ uni-block sample holder system that allows for radiatively heating the substrates.

The substrate samples were then prepared in-situ in a process comprising annealing the substrates in the entry chamber of the reactor at 300° C. overnight, and then further annealing the substrate samples in the preparation chamber of the reactor at 600° C. for 6 hours before the active region layer deposition process began. For substrates consisting of a III-Nitride film or a III-Nitride film deposited upon a substrate, also referred to as a III-Nitride template, an additional step is performed inside the growth chamber of the reactor than consists of annealing the substrate at a temperature between 700 to 900° C. for about 1.5 hours while periodically exposing the surface to a Ga atom flux for about 2 minutes over a 12 minute period so as to cover the substrate surface with metal.

Evaluation of Algan Alloy Active Region Layer Compositions of the Invention:

Room temperature photoluminescence (PL) measurements of devices according to the present invention were performed using a continuous wave 244 nm Ar laser with an excitation power of between 0.4 to 20 mW. Low temperature PL measurements were performed at temperature of between 10K and 300K, by placing samples of devices of the present invention in a He compressor-cooled cryostat. The band gap energy of the films was determined by simulation of reflectivity spectra data obtained by measuring same between 200 and 600 nm using a Perkin Elmer® Lambda 16 UV/VIS/NIR spectrometer, and were confirmed by photorefectance measurements.

The luminescence lifetime of the films was measured by time-resolved photoluminescence (TRPL) measurements taken of the sample for varying fluences (laser pump intensities) using sub-picosecond luminescence downconversion. The surface morphology of the films was investigated by scanning electron microscopy (SEM) using a field emission microscope and cathodoluminescence (CL).

Enhanced Room Temperature Internal Quantum Efficiency in Al<sub>x</sub>Ga<sub>1-x</sub>N Alloys:

The process of the present invention, as described, above was utilized for depositing Al<sub>x</sub>Ga<sub>1-x</sub>N alloy thin films of the present invention directly on sapphire substrates to produce UV LED's according to the present invention, and subsequent measurements of said devices were made as discussed above. For example, FIG. 22 illustrates a comparison of room-temperature photoluminescent (PL) data to reflectivity results for three different representative layers of such Al<sub>x</sub>Ga<sub>1-x</sub>N thin films (i.e., Al<sub>0.45</sub>Ga<sub>0.55</sub>N, Al<sub>0.33</sub>Ga<sub>0.67</sub>N, and Al<sub>0.29</sub>Ga<sub>0.71</sub>N, respectively) deposited using AlN buffer layers on sapphire substrates. The dashed vertical lines represent the approximate band edge, as determined by reflectivity and confirmed by photorefectance measurements.

As clearly illustrated in FIG. 22, the PL peaks of the three Al<sub>x</sub>Ga<sub>1-x</sub>N thin films according to the present invention are significantly red-shifted with respect to the band edge. For these three epitaxial layers, with aluminum percentages of 29%, 33%, and 45%, respectively, the red shifts in PL from band edge are 280 meV, 290 meV, and 400 meV, respectively.

FIG. 22 illustrates that, for bandgaps of the matrix material covering 4.1 eV to 4.8 eV through variation of the Al percentage, the red shift remains ~300 to 400 meV. FIG. 14 shows that the PL intensities of these AlGa<sub>1-x</sub>N active region layers are orders of magnitude brighter than for films with similar defect densities and only band edge emission.

In particular, to further investigate this red-shift effect, PL spectra were taken from 10 K to 292 K on the Al<sub>0.33</sub>Ga<sub>0.67</sub>N sample shown in FIG. 22, and the results thereof shown in FIG. 23. As illustrated therein, at low temperature (i.e., 10K), there are two distinct PL peaks. The red-shifted (RS) peak (3.82 eV, 324.5 nm) shows very bright emission at 10 K that decreases by about a factor of seven as the temperature is increased from 10 to 292 K. The second smaller peak (4.11 eV, 301.5 nm), associated with band edge (BE) emission, is seen at low temperature but, as illustrated, its intensity rapidly decreased by greater than three orders of magnitude from 10 K to 292 K.

Room-temperature monochromatic CL images, as shown in FIG. 5, of the Al<sub>0.33</sub>Ga<sub>0.67</sub>N film shown in FIG. 23, acquired at the RS peak (3.82 eV, 324.5 nm), indicate that luminescence of the Al<sub>0.33</sub>Ga<sub>0.67</sub>N film according to the present invention is spatially nonuniform (2.56×2.56 μm), with feature sizes as small as 100 nm in extent. This image is however limited in its resolution to the diffusion length of the excited carriers at room temperature, which implies that the actual size of these compositional inhomogeneities may be much smaller. This clearly indicates the presence of localized inhomogeneities, i.e., regions of the AlGa<sub>1-x</sub>N film in which the AL is not uniformly incorporated therein. The BE peak has almost no measurable CL signal at room temperature.

The spatial inhomogeneity of the RS CL emission, as illustrated in FIG. 5, and the comparison of the temperature dependence of the band edge (BE) and RS PL peaks, as shown in FIG. 23, suggest both the transport of thermally activated-photogenerated carriers from the wider band gap AlGa<sub>1-x</sub>N matrix into localized states characterized by the longer wavelength emission, as well as the suppression of nonradiative processes in these localized states.

Further evidence of this phenomenon can be seen from investigation of the differences in the two PL peaks shown in FIG. 23, using room temperature time-resolved PL (TRPL) measurements. FIGS. 24 to 26 illustrate the time evolution of the PL intensity measured at the BE peak and the RS peak as a function of fluence for a 290-nm fs laser pulse. As illustrated in FIG. 24, TRPL data for the BE peak shows a prompt response at t=0 and an intensity dependent decay that saturates at higher pump intensity. These decays are characterized by half-lives of from 5 to 30 ps for increasing pump intensities.

TRPL data for the RS peak, however, shows intensity dependent initial rise times with emission peaks at 44, 40, 31, and 21 ps, for increasing pump fluence as shown in FIG. 25. Moreover, the semilog plot illustrated in FIG. 26 shows that the RS peak data possesses nearly intensity independent decays that can be characterized by a fast (~245 ps) and a slow (~590 ps) component, giving a weighted average of ~375 ps.

The slower decay of the BE PL at increased pump fluence, as shown in FIG. 26, shows that carriers are quickly trapped in shallow localized states of the AlGa<sub>1-x</sub>N active region layer that are saturable at high carrier densities (See M. Wraback, F. Semendy, H. Shen, U. Chowdhury, D. J. K. Lambert, M. M. Wong, and R. D. Dupuis, *Phys. Status Solidi A* 188, 807 (2001), which is incorporated herein by reference in its entirety). Further, the overall fast (<30 ps) decays of the BE PL are comparable to those obtained for other AlGa<sub>1-x</sub>N alloys of similar defect density and Al content.

In contrast, localized states of conventional alloys are characterized by bandtails with 20 to 60 meV width for this Al concentration, as well as a large density of deep defect states. Although long lifetimes in bandtail states for conventional AlGa<sub>N</sub> alloys have been reported at temperatures low enough to effect freeze-out of most nonradiative processes, at room temperature the carriers localized in the bandtails of such conventional AlGa<sub>N</sub> alloys subsequently nonradiatively recombine through, or are trapped in, deep states associated with point or structural defects such that the PL decays have little or no spectral dependence.

In contrast, FIG. 26 shows the room-temperature TRPL at the RS peak of the AlGa<sub>N</sub> alloy of the present invention, having localized Al inhomogeneities present therein, to be 290 meV below the band gap, which is strikingly different from its conventional BE counterpart. Since the reflectance data indicates no substantial absorption below the band edge in the AlGa<sub>N</sub> active region layer of the present invention, such that the pump pulse creates carriers primarily in the wider band gap AlGa<sub>N</sub> matrix, the slow rise time corresponds to the transfer of carriers from the surrounding matrix to localized states that participate more readily in radiative than in nonradiative processes through a combination of trap saturation and localization away from bulk defects due to carrier concentration in the nanoscale compositional inhomogeneities. The long PL lifetimes of the RS peak shown in FIG. 26, which are comparable to those observed in conventional materials with up to three orders of magnitude higher dislocation densities, provide further evidence of enhanced radiative efficiency associated with these nanoscale compositional inhomogeneities.

As the carrier density increases, saturation of the localized states causes the transient PL signal at the RS peak to achieve its maximum at earlier times, while the BE TRPL decays become slower due to the filling of both these localized states and the more conventional bandtail states in the wider band gap AlGa<sub>N</sub> matrix. A concomitant blue shift of the time-integrated PL at the RS peak with increasing pump intensity is also observed.

Inventors unexpectedly discovered that a further enhancement of radiative efficiency is attained when using the UV LED of the present invention, through reduction of dislocation and point defect densities in both the higher Al content matrix and the localized regions of the material. In particular, the present inventors produced and tested a double heterojunction (DH) LED structure deposited by MBE on a 1.8 μm-thick Al<sub>0.46</sub>Ga<sub>0.54</sub>N template grown by HVPE on sapphire.

This template has a dislocation density estimated in the mid-10<sup>9</sup> cm<sup>-2</sup> range. A 1 μm Al<sub>0.42</sub>Ga<sub>0.58</sub>N:Si (n~5×10<sup>18</sup> cm<sup>-3</sup>) current spreading layer was grown nearly lattice-matched atop the Al<sub>0.46</sub>Ga<sub>0.54</sub>N template under conditions that inhibit localization. The active region layer consisted of a lightly doped 100 nm Al<sub>0.3</sub>Ga<sub>0.7</sub>N:Si (n~1×10<sup>17</sup> cm<sup>-3</sup>) layer exhibiting localization. The structure was capped with a 10 nm Al<sub>0.42</sub>Ga<sub>0.58</sub>N electron blocking layer. The p-type current spreading layers were omitted for the optical studies.

As illustrated in FIG. 27, the variable temperature PL for the above sample UV LED of the present invention was measured versus photon energy. The intensity of the PL from the localized states in the active region layer was found to only drop by a factor of 3.3 when the temperature was raised from 12 K to room temperature. This finding indicates significantly enhanced radiative efficiency of the UV LED of the present invention versus conventional devices (up to ~30% internal quantum efficiency), due to a combination of the NCI active region layer and reduction of defects in the sample

device relative to structures grown on sapphire. This result is also reflected in the observation that the continuous wave (CW) PL from the above described DH LED structure is 3 to 4 times brighter at room temperature than that from the samples on sapphire.

The foregoing discussion discloses and describes embodiments of the invention by way of example. One skilled in the art will readily recognize from this discussion and from the accompanying drawings and claims, that various changes, modifications and variations can be made therein without departing from the spirit and scope of the invention as defined in the following claims and equivalents thereof.

What is claimed is:

1. A method of manufacturing an ultraviolet light emitting device having a group III-Nitride active layer containing an AlGa<sub>N</sub> alloy having nanometer-scale localized, self-assembled compositionally inhomogeneous regions characterized by having larger or smaller AlN mole fraction than the entire composition on average therein, said method comprising:

depositing an active layer containing an AlGa<sub>N</sub> alloy on a substrate or a film layer formed adjacent a substrate using plasma-assisted molecular beam epitaxy, wherein the deposition of the active layer containing an AlGa<sub>N</sub> alloy is conducted under the following conditions:

- (a) deposition is performed under a faceted growth regime;
- (b) the substrate temperature is maintained within a temperature range of from about 770 to 950° C.
- (c) a nitrogen gas flow rate of from about 0.2 to 1.2 standard cubic centimeters per minute is maintained;
- (d) the active layer containing an AlGa<sub>N</sub> alloy is grown at a rate of about 80 to 1000 nm/hour;
- (e) the Al atom flux as measured by beam equivalent pressure is maintained at from about 1×10<sup>-8</sup> to 2×10<sup>-7</sup> Torr; and
- (f) the Ga atom flux as measured by beam equivalent pressure is maintained at from about 2×10<sup>-7</sup> to 2×10<sup>-6</sup> Torr,

producing an ultraviolet light emitting device having an active layer containing an AlGa<sub>N</sub> alloy having nanometer-scale localized, self-assembled compositionally inhomogeneous regions characterized by having larger or smaller AlN mole fraction than the entire composition on average therein.

2. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is deposited at a rate of from about 80 to 120 nm/hour.

3. The method of manufacturing of claim 1, wherein the nitrogen gas flow rate during the deposition of the active layer containing an AlGa<sub>N</sub> alloy is maintained at from about 0.2 to 0.6 standard cubic centimeters per minute.

4. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is doped with an impurity selected from the group consisting of silicon, magnesium, beryllium, germanium and carbon.

5. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is doped with an impurity selected from the group consisting of silicon, magnesium, beryllium, germanium and carbon in a concentration of about 10<sup>14</sup> to 10<sup>20</sup> atoms/cm<sup>3</sup>.

6. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is doped with silicon in a concentration of about 10<sup>14</sup> to 10<sup>20</sup> atoms/cm<sup>3</sup> and contains an AlN mole fraction of about 33%.



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7. The method of manufacturing of claim 1, wherein: the active layer containing an AlGa<sub>N</sub> alloy is deposited on top of an AlN buffer layer by means of a Ga atom flux, as measured by beam equivalent pressure of from about  $2 \times 10^{-7}$  to  $7 \times 10^{-7}$  Torr.
8. The method of manufacturing of claim 1, wherein: the substrate temperature is maintained within a temperature range of from about 880 to 900° C.
9. The method of manufacturing of claim 1, wherein: the effective nitrogen flux is from 0.09 to 0.238 monolayers/sec.
10. The method of manufacturing of claim 1, wherein: the Al atom flux as measured by beam equivalent pressure is maintained at from about  $1 \times 10^{-8}$  to  $4 \times 10^{-8}$  Torr.
11. The method of manufacturing of claim 1, wherein: the Ga atom flux as measured by beam equivalent pressure is maintained at from about  $3 \times 10^{-7}$  to  $7 \times 10^{-7}$  Torr.
12. The method of manufacturing of claim 1, wherein: the Al atom flux as measured by beam equivalent pressure is maintained at from about  $1 \times 10^{-8}$  to  $3 \times 10^{-8}$  Torr; and the Ga atom flux as measured by beam equivalent pressure is maintained at from about  $2 \times 10^{-7}$  to  $7 \times 10^{-7}$  Torr.
13. The method of manufacturing of claim 1, wherein: the active layer containing an AlGa<sub>N</sub> alloy has AlN mole fraction of from 20 to 80%.
14. The method of manufacturing of claim 1, wherein: the active layer containing an AlGa<sub>N</sub> alloy has AlN mole fraction of from 27 to 60%.
15. The method of manufacturing of claim 1, wherein: the ultraviolet light emitting device has a tunability within the wavelength of from 255 to 340 nm.

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16. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is doped with silicon at a concentration of up to  $10^{19}$  atoms/cm<sup>3</sup>.
17. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is doped with silicon at a concentration of about  $2 \times 10^{17}$  atoms/cm<sup>3</sup>.
18. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is characterized by having regions in which the aluminum is not uniformly incorporated therein.
19. The method of manufacturing of claim 1, wherein the nanometer-scale localized compositionally inhomogeneous regions have a band-gap energy less than the surrounding material.
20. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy has an AlN mole fraction of from 27 to 40 percent.
21. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy has an AlN mole fraction of from 27 to 33 percent.
22. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy is deposited within the active regions of a light emitting semiconductor stack.
23. The method of manufacturing of claim 1, wherein the active layer containing an AlGa<sub>N</sub> alloy deposited under a faceted growth mode is characterized by a fine scale, faceted surface morphology having surface pits on the order of about 10 to 100 nm wide.

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